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to

National Aeronautics and Space Administration
Ames Research Center

FLAMMABILITY SCREENING TESTS
OF RESINS

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EXECUTIVE SUMMARY

Forward

This report describes research which has been conducted by the
Flammability Research Center of the University of Utah for the National
Aeronautics and Space Administration, Ames Research Center, Moffett
Field, California under research contract #NAS 2 9950. The subject of
the research was the evaluation of selected flammability characteristics
of glass cloth laminates of thermosetting resins.

The following is a summary presentation of the research results.
The purposes of the summary are to highlight specific objectives and
results of the project without presenting the details of experimental
procedures or uncondensed data. An unabridged presentation of the work
follows this summary.

Introduction

The objective of this research was to develop a protocol for the
evaluation of the flammability hazards presented by glass cloth lamin-
ates of thermosetting resins and to demonstrate the usefulness of that
protocol with the two laminates which were the subject of the study.
The materials studied were the glass laminates of an epoxy resin, MY-
720, and a bismaleimide resin, M-751. The protocol consisted of four
components:

1. Determination of smoke generation from the laminates;

2. Analysis of products of oxidative degradation of the
   laminates;

3. Determination of the minimum oxygen concentration necessary to maintain flaming oxidation of the laminates as a function of radiant energy impinging upon the laminate (this value of oxygen concentration is defined as the oxygen extinguishment index or OEI) and;

4. Evaluation of the toxicological hazard of the combustion products of the laminates.

The combination of results from each of the four components of the protocol provides a sophisticated and realistic assessment of the flammability hazards of glass laminates.

Section I

Smoke Evolution from Glass Laminates of an Epoxy Resin MY-720

and a Bismaleimide Resin M-751

Smoke generation under flaming conditions at 2.5 and 5.0 watts/cm^2 of radiant heat flux was determined in the NBS-Aminco Smoke Density Chamber for the two laminates. The bismaleimide resin M-751 gave dramatically lower values of maximum specific optical densities (Dm) at both heat fluxes. At 2.5 watts/cm^2 the Dm of M-751 was 1/3 to 1/2 that of M-720. At 5.0 watts/cm^2 the Dm of M-751 was 1/4 that of MY-720.

Section II

Analysis of Volatile Organic Compounds Produced From the

Combustion of Glass Laminates of an Epoxy Resin MY-720

and a Bismaleimide Resin M-751

Combustion atmospheres were generated using a conductive heat furnace into a 60 ℓ exposure chamber. The atmospheres were sampled

by exhausting the gas atmosphere through a cooled (0°) tube packed with porous polymer adsorbent. The adsorbent tube was transferred to a specially modified inlet of the gas chromatograph/ mass spectrometer system. The trapped volatile products were desorbed at 200°C and swept onto the head of the GC column. The column eluent was split between a flame ionization detector and the mass spectrometer (via a jet separator). Degradation products from both the flaming and nonflaming modes of combustion were determined for both laminates. The analytical procedure was designed to detect volatile organic compounds. Products such as HCN, CO and CO_2, which were determined during the toxicological evaluation as part of that protocol, are reported in Section IV of this summary.

The volatile organic compounds from the nonflaming combustion of the epoxy laminate MY-720 consisted mostly of C_3 molecules and a number of benzene derivatives. For example, acetone was a major product, probably originating from the 1, 3-substituted isopropanol moieties of the cured resin. Other C_3 products included propene nitrile and propene-3-ol. There were also appreciable quantities of C_4 molecules, methyl-ethyl-ketone being a major one. The formation of C_4 products requires complex mechanisms involving radical combination reactions, since there are no aliphatic C_4 units in the cured resin. The aromatic materials consisted mostly of benzene, toluene, xylene, styrene, and benzonitrile. These compounds arise via an assortment of mechanisms of varying complexity involving the 1,4-substituted phenyl group which is plentifully distributed throughout the polymer. SO_2 was also detected. This presumably originated from the SO_2 moiety of the curing agent, 4, 4-diamino-diphenyl-sulfone.

The products from the flaming combustion of MY-720 varied from the nonflaming combustion in quantity rather than identity. The ratio of aromatic to aliphatic compounds increased dramatically during flaming combustion. None of the volatile organic products observed during either flaming or nonflaming combustion of MY-720 were likely to be primary toxicants.

The combustion of the bismaleimide resin M-751, in both the flaming and nonflaming modes, resulted in a lower overall yield of volatile organic compounds than did combustion of the MY-720 resin. In the nonflaming mode major products were ethanol, benzene, toluene, xylene, benzonitrile, and N-methyl-2-pyrrolidone. The latter is used as a solvent for the resin during prepreg formation. There was nearly a complete absence of C_3 and C_4 molecules, reflecting the absence of acyclic C_3 and C_4 aliphatic moieties in the cured resin. The aromatic materials originated from the substituted aromatic groups in the cured resin. Ethanol probably originated from the maleimido portion of the resin polymer via a complex mechanism. In comparison to the MY-720 resin, it is noteworthy that flaming oxidation of M-751 did not result in a radically different product distribution. As with the MY-720 resin, the volatile organic products from combustion of M-751 were not likely to be primary toxicants.

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Section III

Oxygen Extinguishment Indices of Glass Laminates of an Epoxy Resin MY-720 and a Bismaleimide Resin M-751 Under Simultaneous Exposure to Radiant Heat

An instrument for the determination of oxygen extinguishment indices as a function of radiant energy was constructed. The oxygen extinguishment index (OEI) at a given radiant energy was defined as the minimum concentration of oxygen which will maintain flaming oxidation of a specimen exposed to the given flux of radiant energy. Samples were exposed in the vertical plane to the energy flux since this configuration was assumed to be representative of the most probable end-use configuration. The OEI values of the two glass laminates were determined at 0, 2.5, and 5.0 watts/cm^2 of radiant energy. There were no significant differences in the OEI values of the two materials over the range of applied radiant energies.

Section IV

Toxicological Evaluation of the Combustion Products of Glass Laminates of an Epoxy Resin MY-720 and a Bismaleimide Resin M-751

The toxicities of the combustion products of the two resin systems were compared in the rat using a small-scale laboratory furnace/exposure system. It was found that there was no significant difference between the toxicological potencies of the combustion

products of the two resins, when compared under worst-case conditions, in terms of both their incapacitating and lethal effects in the rat. The causality of the observed toxicity of the combustion products of both materials was explained for the most part by the presence of both CO and HCN in the combustion product atmospheres. Neither material produced any unusually toxic or highly potent combustion products other than those normally encountered.

There was some evidence that survival time on exposure to the nonflaming combustion products of the bismaleimide resin may be greater than for the epoxy resin. This was due to a delay in the generation of both CO and HCN from the bismaleimide resin. The effect may have some importance when considering occupant survivability in the post-crash scenario in aircraft.

TABLE OF CONTENTS

FORWARD

This report describes research which has been conducted by the Flammability Research Center of the University of Utah for the National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California under research contract #NAS 2 9950.

The research was an evaluation of selected flammability characteristics of two thermosetting glass laminate composites. The overall objective of the research was to develop a protocol for the evaluation of the flammability hazards that these materials might pose in real fires and to demonstrate the usefulness of that protocol by the study of two laminate materials. The work described in this report consisted of four areas of investigation:

1. Smoke generation.

2. Analysis of products of combustion.

3. Determination of oxygen extinguishment values.

4. Toxicological evaluation of combustion products.

Accordingly, the report is presented in four chapters which deal with each of the above areas. The report is preceeded by an overall introduction and succeeded by overall conclusions to lend continuity to the total project. The chapters have been presented as self-contained units which can be read separately and in any order.

INTRODUCTION

The objective of this research was to develop a protocol for the evaluation of the flammability hazards presented by glass cloth laminates of thermosetting resins and to demonstrate the effectiveness of this protocol with the two laminates which were the subject of this study. The investigation involved the glass laminates of the two materials identified below:

MY-720: epoxy resin based on methylene dianiline, cured with diamino diphenyl sulfone (DDS).
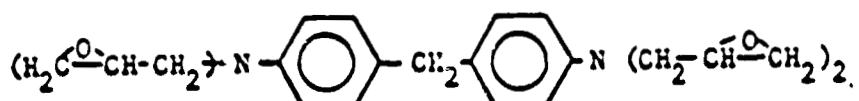
MY 720

M-751: bismaleimide resin based on the reaction of m-maleimidobenzoic acid chloride with 4,4'-diaminodiphenyl-methane, cured by heating to temperatures of 180 to 240°C (the curing reaction probably involves free radical polymeri zation of the double bonds of the maleimide groups).
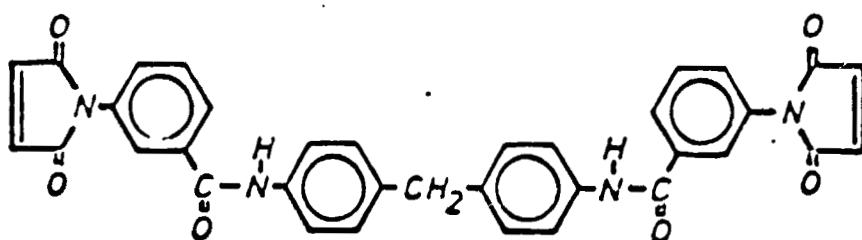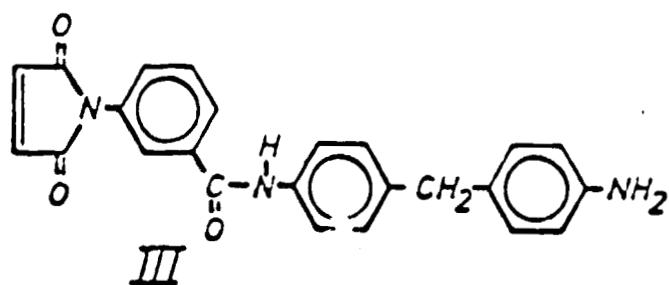
M 751

The resin content of the laminates was 30 to 40 percent.

The protocol consisted of four components:

1. Determination of smoke generation from the glass laminates.

2. Analysis of products of flaming and nonflaming oxidative degradation of the glass laminates.

3. Determination of the minimum oxygen concentration necessary to maintain flaming oxidation of the laminates as a function of radiant energy impinging upon the laminate (this value of oxygen concentration is defined as the oxygen extinguishment index or OEI).

4. Evaluation of the toxicity of the combustion products of the laminates using a protocol developed at the Flammability Research Center.

The combination of results from each of the four components of the protocol provides a sophisticated and realistic assessment of the flammability hazards of glass laminates.

OVERALL CONCLUSIONS

The performance of two glass laminate resin systems has been studied in a range of flammability tests. The tests were designed to establish the potential threat to exposed personnel in terms of smoke generation and the toxicity of combustion products in the event that the materials were involved in a fire, with specific reference to the post-crash fire scenario in aircraft.

The determination of oxygen extinguishment indices of the two resin systems showed no significant difference between the materials. This result suggested that the likelihood of the two materials becoming actively involved in an existing fire was approximately equal. The measurement of smoke generation in the NPS Smoke Chamber showed that the bismaleimide resin outperformed the epoxy resin in every parameter studied. This suggested that the hazards associated with smoke generation were likely to be less with bismaleimide resin than with the epoxy resin. There was no significant difference in the potency of the combustion products of the two materials, when compared under worst-case conditions. Neither resin produced an unusually toxic or highly potent combustion product other than those normally encountered. There was some evidence that the potential survival time might be somewhat greater for the bismaleimide resin combustion products when compared to the epoxy resin combustion products. This was due to a delay in the generation of the primary toxicants, and may be particularly important in aircraft fires.

The experiments suggested, therefore, that the bismaleimide resin was superior to the epoxy resin when considering the overall range of flammability properties of the two materials.

SECTION I

Smoke Evolution from Glass Laminates of an Epoxy Resin MY-720

and a Bismaleimide Resin M-751.

R. W. Arhart

Section I

Smoke Evolution from Glass Laminates of an Epoxy Resin MY-720

and a Bismaleimide Resin M-751.

Smoke generation under flaming conditions at 2.5 and 5.0 watts/cm^2 of radiant heat flux has been determined in the NBS-Aminco Smoke Density Chamber for the glass laminates of the two materials identified below:

1. MY-720: epoxy resin based on methylene dianiline, cured with diamino diphenyl sulfone (DDS).
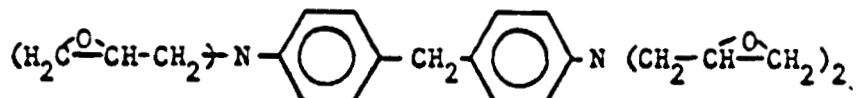
MY 720

2. M-751: Bismaleimide resin based on the reaction of m-maleimidobenzoic acid chloride with 4,4'-diaminodiphenyl-methane.

M 751
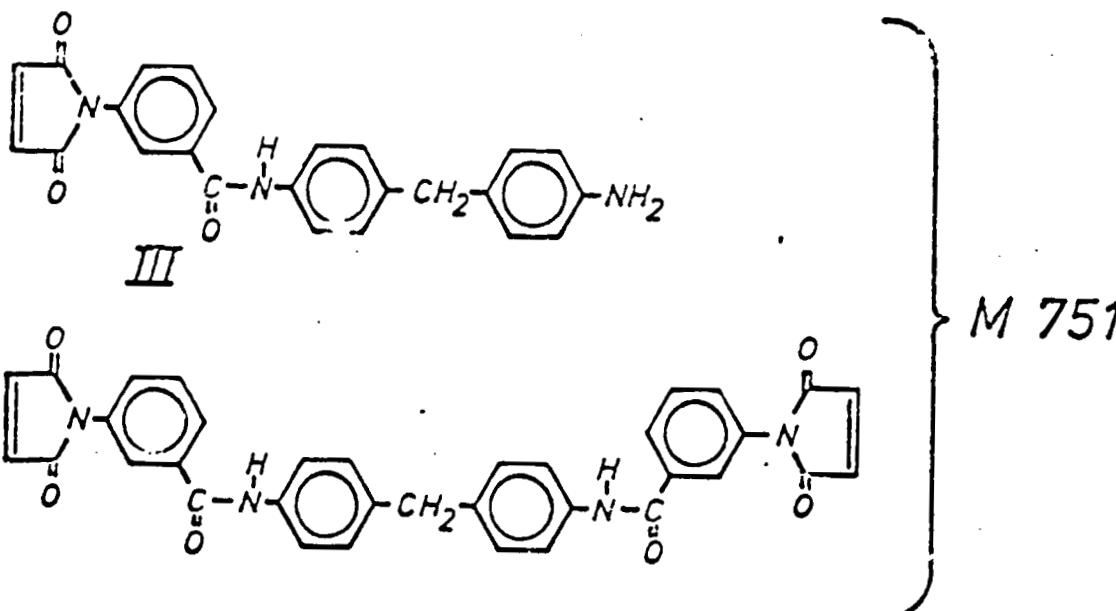
The smoke parameters are presented in Tables I and II. Each material was tested in duplicate rather than the recommended triplicate in order to preserve material for other phases of the project. The data for the duplicate runs were in good agreement. The smoke parameters reported in Tables I and II are the maximum specific optical density (Dm), the time to reach Dm (Tm), the time to reach D_{16} (T_{16})*, and the final mass optical density (FMOD). The latter parameter is one which has been suggested by Seader and Chien as being representative of the efficiency of smoke generation from a material as a function of mass volatilized from the material [1]. The mass optical density is the specific optical density divided by the mass loss of the material (Ds/Δm). The mass optical density therefore describes the amount of smoke generated per unit mass loss.

As can be seen in Tables I and II, the M-751 laminate dramatically outperforms the MY-720 laminate in every parameter. Furthermore, it was observed at both 2.5 and 5.0 watts/cm^2 that the MY-720 laminate flamed much more vigorously than the M-751 laminate. The difference in behavior of the two resins is particularly interesting since the mass losses from each of the resins were about equal. Thus there is a signficant difference in the FMOD values.

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*D=16 corresponds to 75% transmittance.

[1] J. D. Seader, W. P. Chien, "Qualification and Measurement of Smoke," paper presented at the Polymer Conference Series, Flammability Characteristics of Materials, University of Utah, Salt Lake City, Utah, July 1973.

TABLE I

SMOKE EVOLUTION

2.5 watts/cm², flaming

SAMPLE	SAMPLE WEIGHT (g)	SAMPLE THICKNESS (mm)	WEIGHT LOSS (g)	Dm	T_m (min)	T_{16} (min)	FMOD Dm/Δm
M-751	31.5	3.3	4.5	64	14	4.1	14.2
	32.5	3.3	4.4	54	14	4.5	12.3
MY-720	29.1	2.8	4.4	132	8.0	1.5	30.0
	27.6	2.8	5.6	174	8.0	1.5	31.1

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TABLE II

SMOKE EVOLUTION
5.0 watts/cm², flaming

SAMPLE	SAMPLE WEIGHT (g)	SAMPLE THICKNESS (mm)	WEIGHT LOSS (g)	Dm	T_m (min)	T_{16} (min)	FMOD Dm/Δm
M-751	31.1	3.3	7.4	109	11.0	2.0	14.7
	31.0	3.3	7.1	105	10.0	3.0	14.8
MY-720	27.8	2.8	5.6	430	3.0	0.8	76.8
	25.9	2.8	4.6	425	4.0	0.8	92.4

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SECTION II

Analysis of Volatile Organic Compounds Produced from the

Combustion of Glass Laminates of an Epoxy Resin MY-720

and a Bismaleimide Resin M-751.

B. M. Hughes
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Section II

Analysis of Volatile Organic Compounds Produced from the
Combustion of Glass Laminates of an Epoxy Resin MY-720
and a Bismaleimide Resin M-751.

Combustion atmospheres from the two materials were generated using a conductive heat furnace into a 60 ℓ exposure chamber. The atmospheres were sampled directly by exhausting the chamber atmosphere through a particulate filter (40 μM) and then through a stainless steel "U"-shaped tube that was cooled to 0°C. The tube contained 0.25 grams of porous polymer adsorbent that retained the volatile organic compounds from the combustion atmosphere. The gas sampling began at three mintues after initiation of combustion and continued for eight minutes at a flow rate of 150 ml/min, giving a total sample volume of 1.2 liters.

The adsorbent tube was transferred to a specially modified inlet of the gas chromatograph/mass spectrometer system (Hewlett-Packard model 7620A research chromatograph interfaced to a Hewlett-Packard model 5930A mass spectrometer with the Hewlett-Packard model 2100S minicomputer for data acquisition). The trapped volatile gases were desorbed at 200°C and swept into the gas chromatographic column for separation. The effluent was split between a flame ionization detector (FID) and a glass jet separator. The latter was used for enrichment of the eluate before introduction into the ion source of the mass spectrometer. The FID response was standardized by injecting known quantities of butane and recording peak areas using a Hewlett-Packard model 3352B laboratory data system.

The quantity, C_x, of a given compound, x, analyzed in the trapped sample is dependent upon four variables according to the expression:

$$C_x = \frac{SA_x R_x}{T_x}$$

Where:
S = sensitivity of the GC, as determined by injection of n-butane,

A_x = GC peak area of compound x,

R_x = relative GC detector response factor of compound x, and

T_x = relative trapping efficiency of x.

In these experiments, published response factors [1] are used for known compounds and the assumption is made that the response factor of each unidentified compound is equal to that of n-butane. In addition, it is assumed that the trapping efficiency of each compound is equal to 1. The total amount of compound x produced in the combustion of materials is calculated from the amount analyzed in the trapped sample by multiplying C_x by the ratio of the total chamber volume to the trapped volume. Since the molar response of each component is assumed to be equal to that of n-butane, the total amount of each compound produced, in milligrams, is given by:

$$C_{x, total} = (R_x/R_s)(A_x/A_s) \cdot 0.505 \text{ milligrams}$$

Where: A_x = GC peak area of n-butane inject (0.5 ml of 1% standard)

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MY-720/DDS Combustion Products

Degradation products from the flaming and nonflaming modes of combustion were determined for the epoxy resin based on glycidyl ether of methylene dianiline (I) cured with 4,4'-diamino-diphenyl-sulfone (II).

$$(H_2C\text{-}CH\text{-}CH_2)\text{-}\overset{H}{N}\text{-}\phi\text{-}CH_2\text{-}\phi\text{-}\overset{H}{N}\text{-}(CH_2\text{-}CH\text{-}CH_2)_2$$

(I)

$$NH_2\text{-}\phi\text{-}SO_2\text{-}\phi\text{-}NH_2$$

DDS

(II)
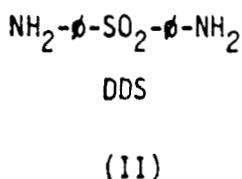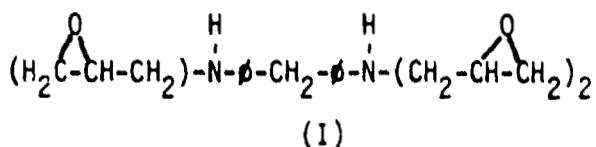
Fiberglass laminates were supplied by NASA and combusted in the conductive heat furnace that was used in the study of the toxicity of the combustion products of the two materials (Section IV). Figures 1 and 2 show the GC/MS/computer analysis of nonflaming combustion products formed at 600°C and the flaming combustion products formed at 680°C. The major identified products have been indicated on the Figures for clarity. The ethanol product shown in Figure 2 is an artifact of the experiment and is produced from the ethanol which is added to the sample to ensure flaming combustion. As discussed in the previous section, the flame ionization response was used to obtain quantitative information on these combustion mixtures and is summarized in Table I. Values in parentheses in the table are corrected for the relative flame ionization response of the identified compound. Detailed mass spectra for each compound listed in the table are given in Appendix A.

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The total areas of the compounds listed in the table are more than 90% of the total areas measured with the flame ionization detector/ integrator system used for this study. As mentioned above, the par- enthetical values given in the table are quantitated values using the published flame ionization response factors relative to n-butane. The corrections made at most a difference of a factor of three in the amount of compound measured and the data for all hydrocarbons shown in this table should be within this degree of accuracy. However, since SO_2 does not give a signficant flame ionization response, no attempt has been made to quantitate this degradation product from the data. Levels of SO_2 were subsequently determined to be less than 100 ppm using standard chromatographic techniques.

The mechanistic speculation required to relate the products in Table I to the cured resin vary from the straightforward to the extre- mely oblique. For example, starting at the top of the table, sulfur dioxide originates from the DDS portion of the polymer. The mechanism of its elimination may vary from concerted to homolytic cleavage of carbon-sulfur bonds. In either case, the driving force for the reaction is the elimination of the very stable molecule SO_2. It is probable that this is a relatively low temperature process and may be one of the first processes to occur in the degradation of the polymer. The formation of the C_4 molecules, butadiene, butyne, and methyl ethyl ketone, require complex mechanisms of bond scission and recombination since there are no aliphatic 4-carbon units in the polymer. Acetone arises from the 1,3- disubstituted propanol units in the cured polymer. These units are formed during the curing process by reaction of the amine curing agent

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with the primary carbon of the glycidyl ether unit. Propene nitrile and propene-3-ol also probably arise from the isopropanol units. In the case of propene nitrile, addition of a nitrile radical to the 3-carbon unit is required. A nitrile radical is a probable species in the thermal degradation of this material because of the presence of non-aromatic nitrogen in both the methylene dianiline and DDS units. Benzene derives from the 1,4-substituted phenyl groups which are plentifully distributed throughout the polymer. Toluene probably originates predominantly from the methylene dianiline units. Xylene, styrene and benzonitrile require complex mechanisms of formation which probably involve radical addition to phenyl groups. It is interesting to note the large amounts of styrene and benzonitrile formed in the flaming mode. No rationalization for this observation is offered. The formation of pyridine requires considerable mechanistic gymnastics. However, as with all unsubstituted aromatic species, the very stability of the molecule is the major factor contributing to its formation.

M-751/DDS Combustion Products

Degradation products from the flaming and nonflaming modes of combustion were determined for the resin system based on the reaction of m-maleimidobenzoic acid chloride (I) with 4,4'-diaminodiphenylmethane (II). The resin consists of a mixture of III and IV, the relative amounts of III and IV being governed by the stoichiometry of the reaction of I and II. The material is cured by heating to approximately 200°C, which affects free radical polymerization of the ethylene units of the N-substituted maleimide groups.

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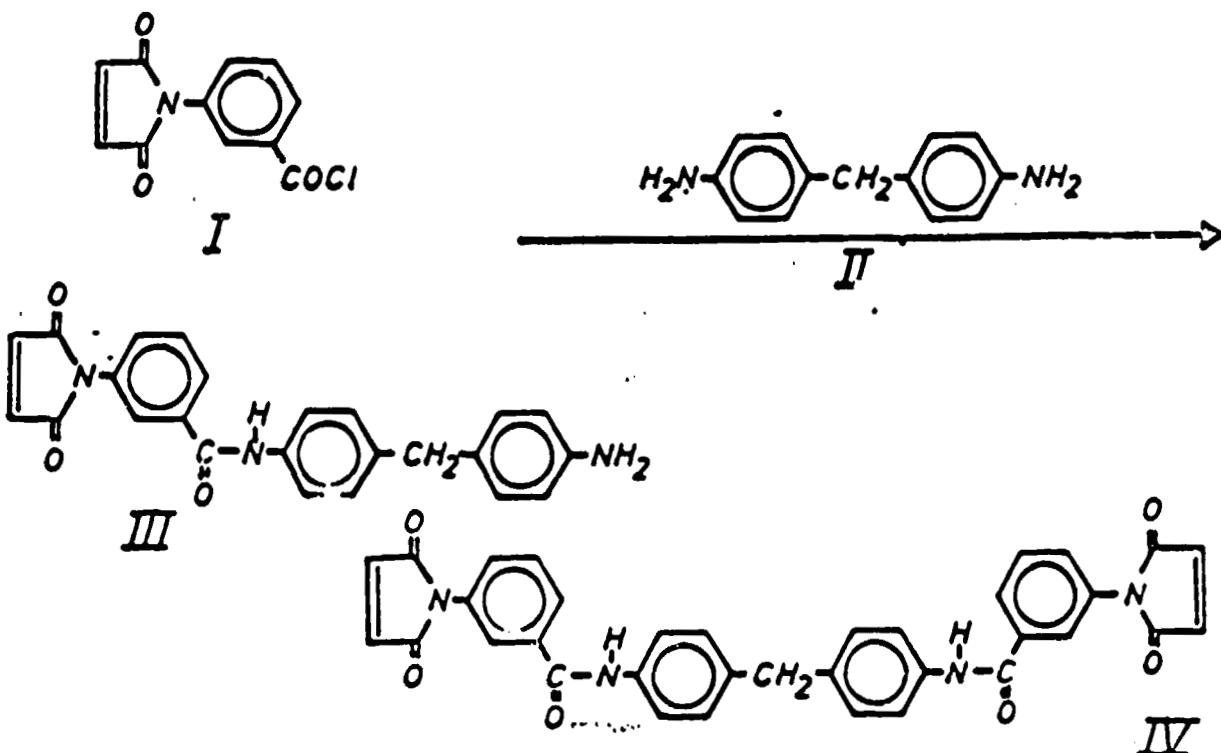
Fiberglass laminates were supplied by NASA and combusted in the conductive heat furnace. Figures 3 and 4 show the GC/MS/computer analysis of nonflaming combustion products formed at 490°C and the flaming combustion products formed at 700°C. The major products have been identified on the figures for clarity.

The ethanol products shown in Table II, unlike that in Table I, arise from the degradation of the M-751 system, as well as from the solvent added to ensure flaming combustion. Discrete spectra, upon which the identifications in Table II are based, are compiled in Appendix A.

Comparison of the products from the epoxy resin (Table I) and the bismaleimide resin (Table II) reveals some similarities. For example, benzene, toluene, xylene, and benzonitrile are major products from each resin. In the M-751 resin these compounds arise from the phenyl groups of the methylene dianiline units, which are common to both resins. The

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M-751 resin produced no acetone because of the absence of 1,3-disubstituted isopropanol units. Residual N-methyl-2-pyrrolidone, which was used as a solvent in prepreg formation, was volatilized during the thermal degradation and appears as one of the major components of the combustion atmosphere. Sulfur dioxide and carbon disulphide were observed in the atmosphere from nonflaming degradation (see Figures 3 and 4). The observation of SO_2 and CS_2 in either degradation mode was not expected because the resin nominally contained no sulfur. The validity of the observation of sulfur species in the flaming mode of degradation of M-751 is in doubt.

The total areas of the chromatographable compounds listed in Table II also exceed 90% of the total compounds chromatographed. More precise absolute data is given in parentheses in Table II for those compounds which have known flame ionization responses.

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[1] W. A. Dietz, *J. of Gas Chrom.*, pp. 68-71 (1967).

Table I

Quantitative Analysis of Combustion Products Formed in the Nonflaming (600°C) and Flaming (680°C) Combustion of MY-720/DDS Glass Laminates

Retention Time Minutes	Compound	Amount Produced (mg butane/gm)	
		Nonflaming	Flaming
7.0	sulfur dioxide	N.Q.[a]	N.Q.
9.88	isobutene	0.24	--
10.15	1,3-butadiene/butyne	0.29	--
10.70	ethanol	--	3.95
12.20	acetone	1.39 (3.1)[b]	0.29 (0.64)
13.02	carbon disulfide	0.15	0.29
13.07	propene nitrile	0.18	--
13.33	propene-3-ol	0.59	--
14.40	methyl-ethyl-ketone	0.77	--
15.90	benzene	1.26 (1.65)	3.02 (3.93)
16.45	N.I.[c]	0.25	--
17.48	N.I. (MW = 84)	0.11	--
18.00	toluene	1.14 (2.2)	0.72 (1.39)
18.54	pyridine	0.28	--
19.86	N.I. (MW = 104)	--	0.2
20.12	xylene	0.54 (1.1)	--
21.36	sytrene	0.25	1.36
22.36	N.I. (MW = 106)	0.10	--
23.06	N.I.	0.15	--
25.50	benzonitrile	0.46 (1.0)	0.96 (2.11)
25.61	N.I.	--	0.34
26.91	N.I.	--	0.19

[a]N.Q. - not quantified

[b]values in parentheses are corrected for relative flame ionization responses for butane and the identified compound

[c]N.I. - not identified

Table II

Quantitative Analysis of Combustion Products Formed in the
Nonflaming (490°C) and Flaming (700°C) Combustion of
M-751 Glass Laminates

Retention Time Minutes	Compound	Amount Produced (mg butane/gm)	
		Nonflaming	Flaming
8.0	sulfur dioxide	N.Q.[a]	N.Q.
12.0	ethanol	0.2 (0.38)[b]	0.31 (0.58)
13.4	isobutane/butane/propanol	0.06	--
13.5	acetone	--	0.06 (0.13)
14.3	carbon disulfide/propenenitrile	0.02	0.09
14.4	N.I.[c]	0.01	--
15.8	methyl ethyl ketone	0.01 (0.02)	0.03 (0.07)
17.3	benzene	0.78 (1.0)	0.84 (1.1)
17.9	N.I. (MW = 100)	0.05	--
18.0	methacrylonitrile/vinyl acetonitrile	--	0.01
18.9	4-methyl-2-pentanone/2-hexane/ methyl isobutyl ketone	0.15	0.02
19.4	toluene	0.68 (1.31)	0.24 (0.46)
21.2	xylene	0.14 (0.27)	0.04 (0.08)
22.9	N.I.	0.06	--
24.0	N.I.	0.08	--
25.1	benzonitrile	0.35 (0.68)	0.23 (0.51)
26.7	N.I. (MW = 116)	0.08	0.02
28.3	2-methyl-pyrrolidone	0.82	0.13
29.3	N.I. (MW = 117)	--	0.04
35.3	N.I. (MW = 128)	--	0.05

[a]N.Q. - not quantified

[b]values in parentheses are corrected for relative flame
ionization responses for butane and the identified
compound

[c]N.I. - not identified
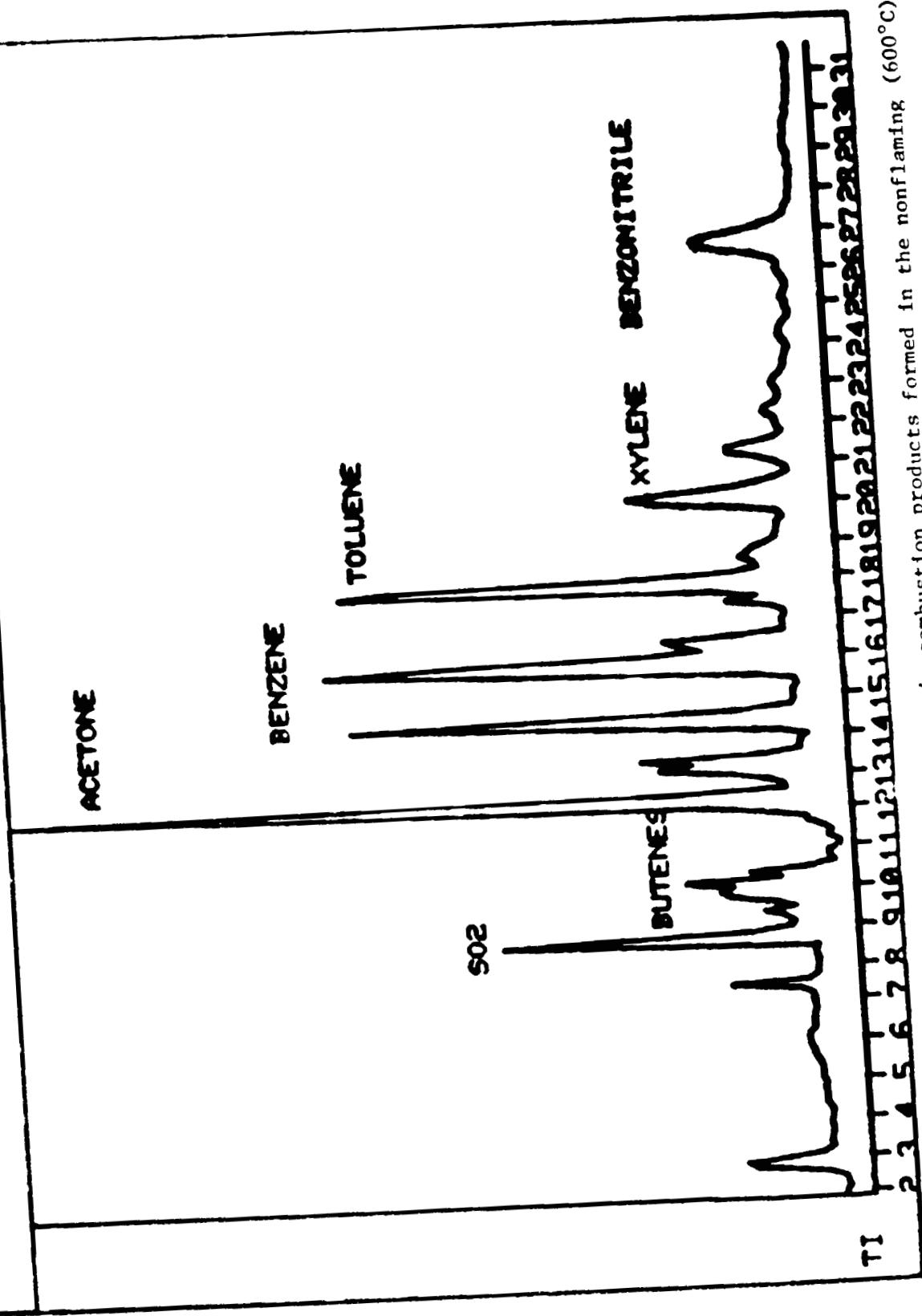
Figure 1. GC/MS/computer analysis of organic combustion products formed in the nonflaming (600°C) combustion of the NY 720/DDS epoxy system.
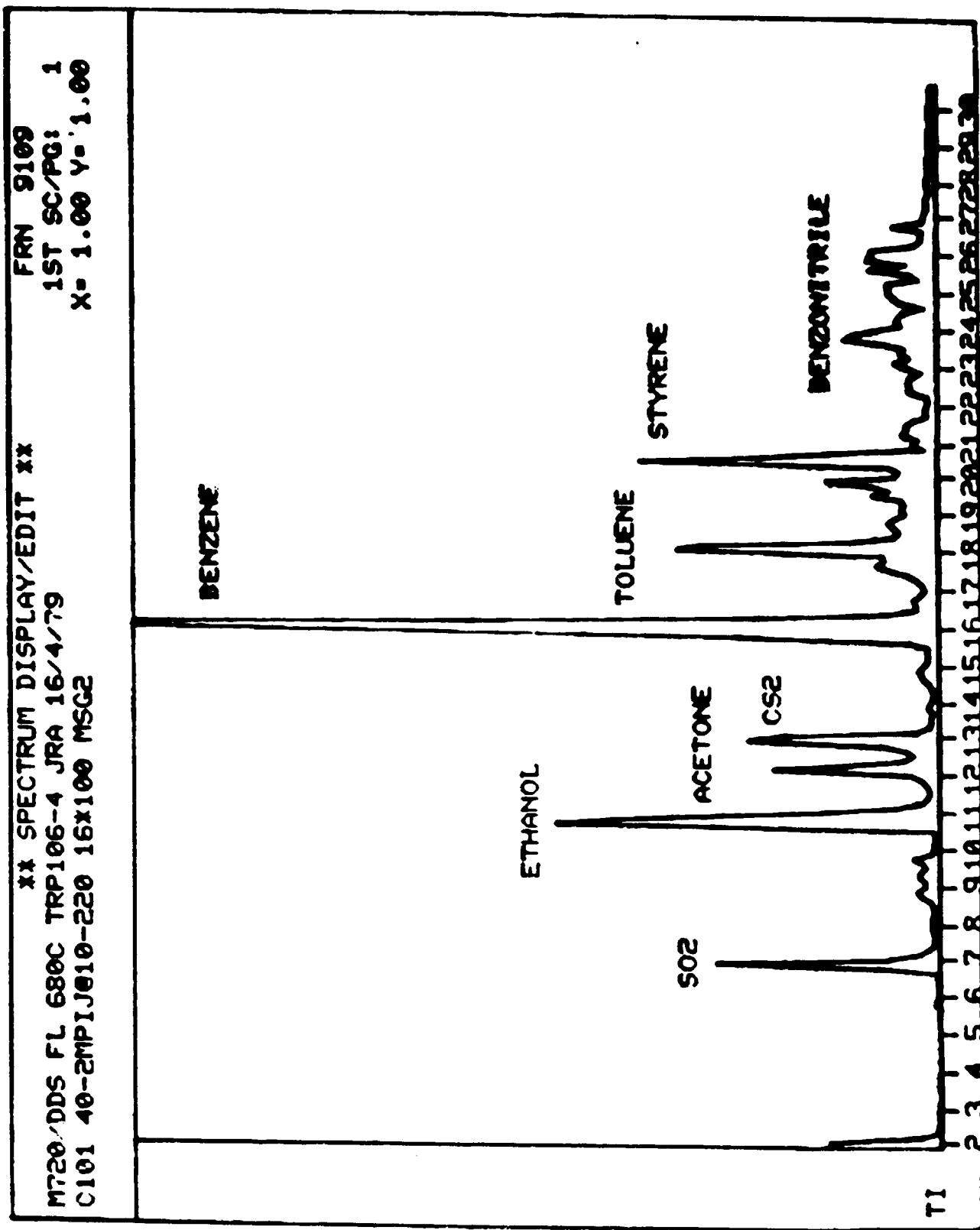
Figure 2. GC/MS/computer analysis of organic combustion products in the flaming (680°C) combustion of the MY 720/DDS epoxy system.
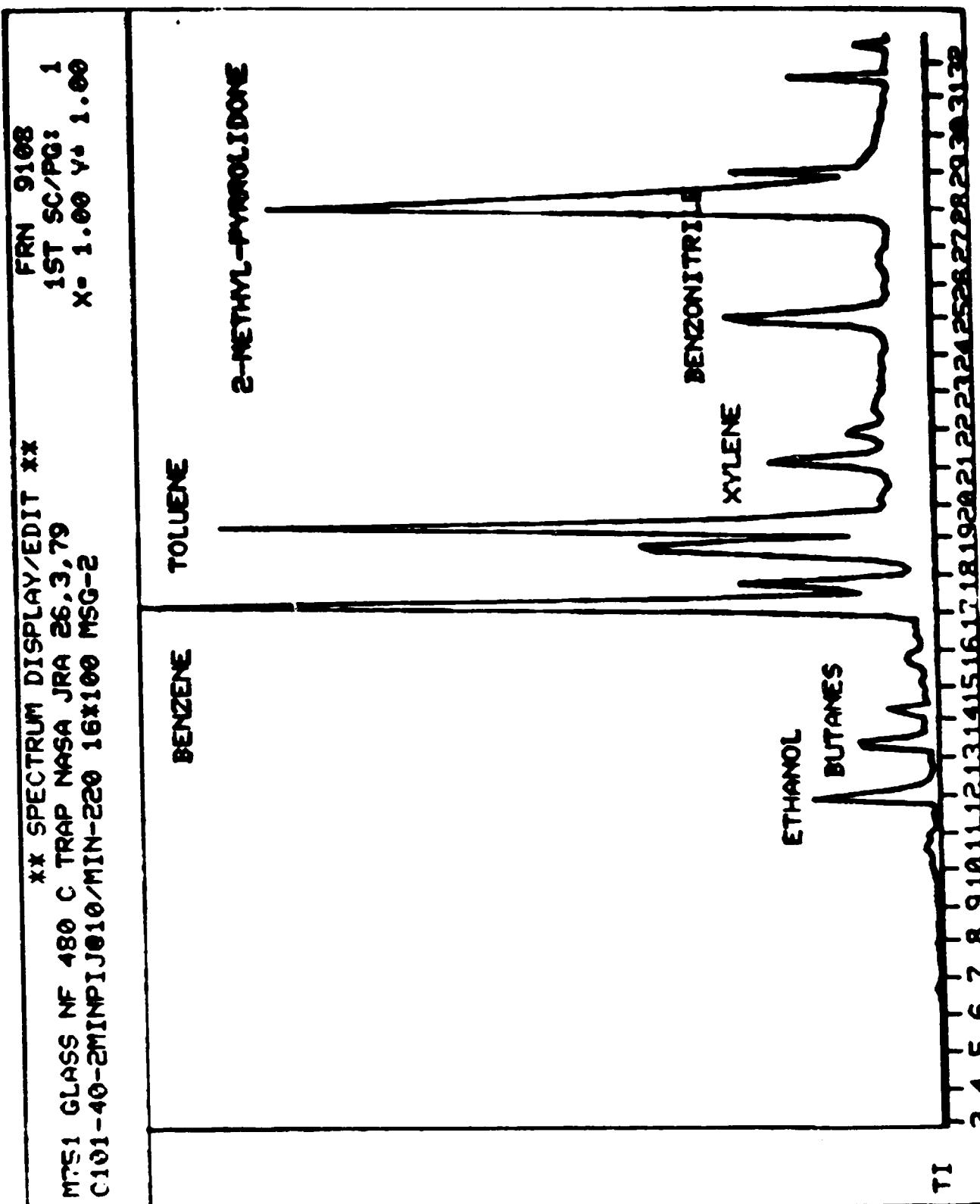
Figure 3. GC/MS/computer analysis of organic combustion products in the nonflaming (490°C) combustion of the M 751 resin system.
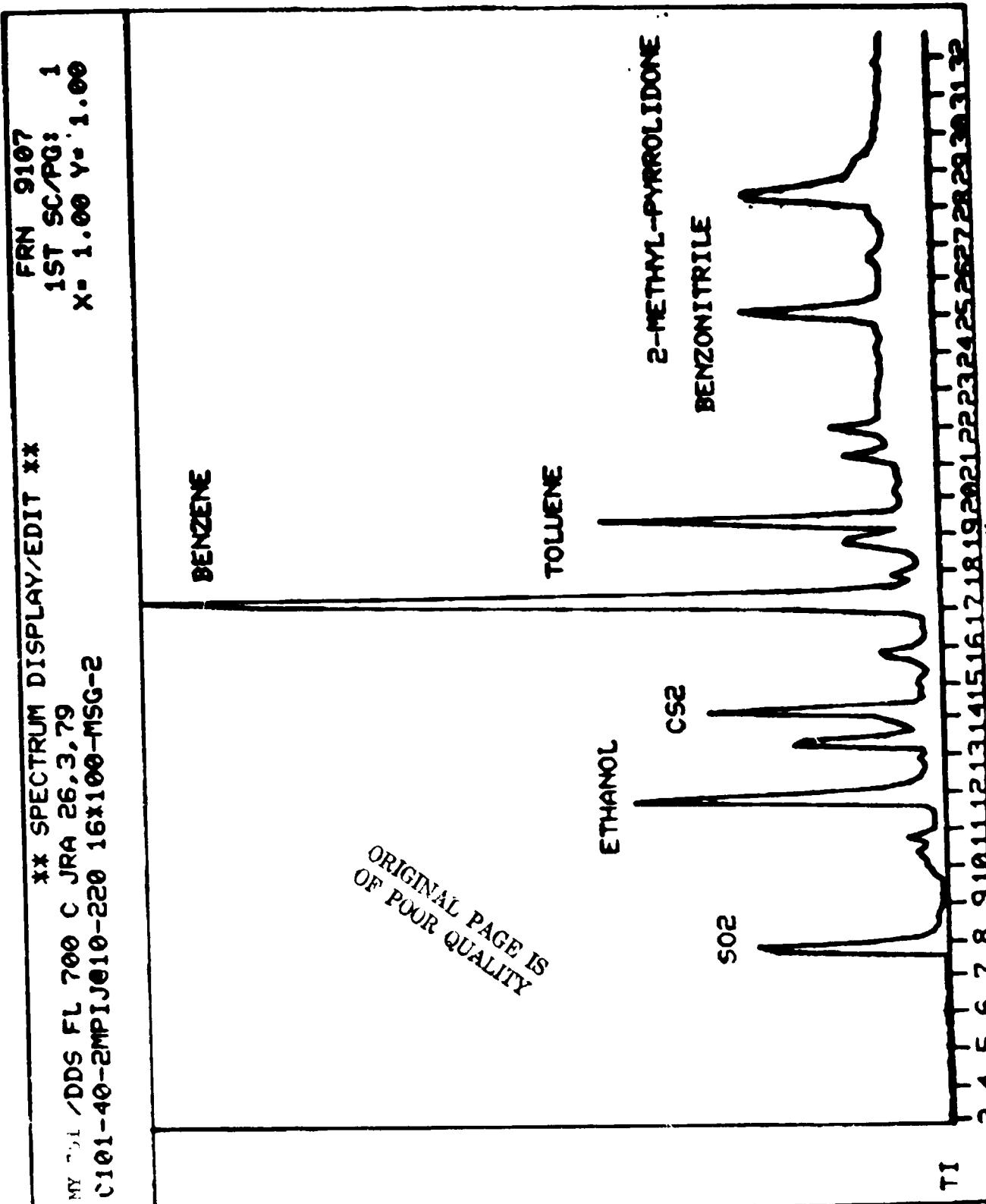
Figure 4. GC/MS/computer analysis of organic combustion products in the flaming (700°C) combustion of the M 751 resin system.

Appendix A

MASS SPECTRA OF COMPONENTS IDENTIFIED AS COMBUSTION PRODUCTS
IN TABLES I AND II
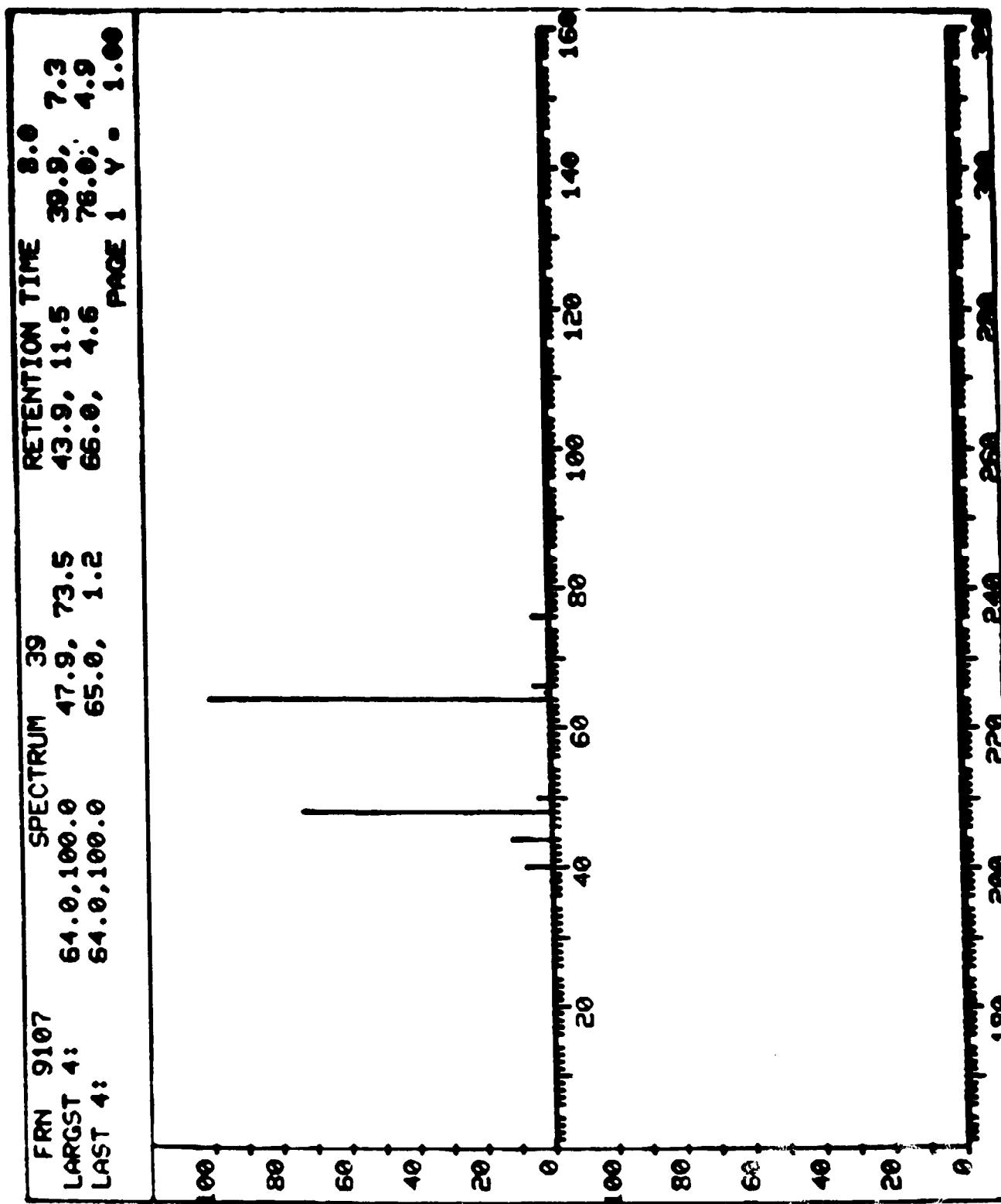
Figure A-1. Mass spectrum of SO_2 reported in Tables I and II.
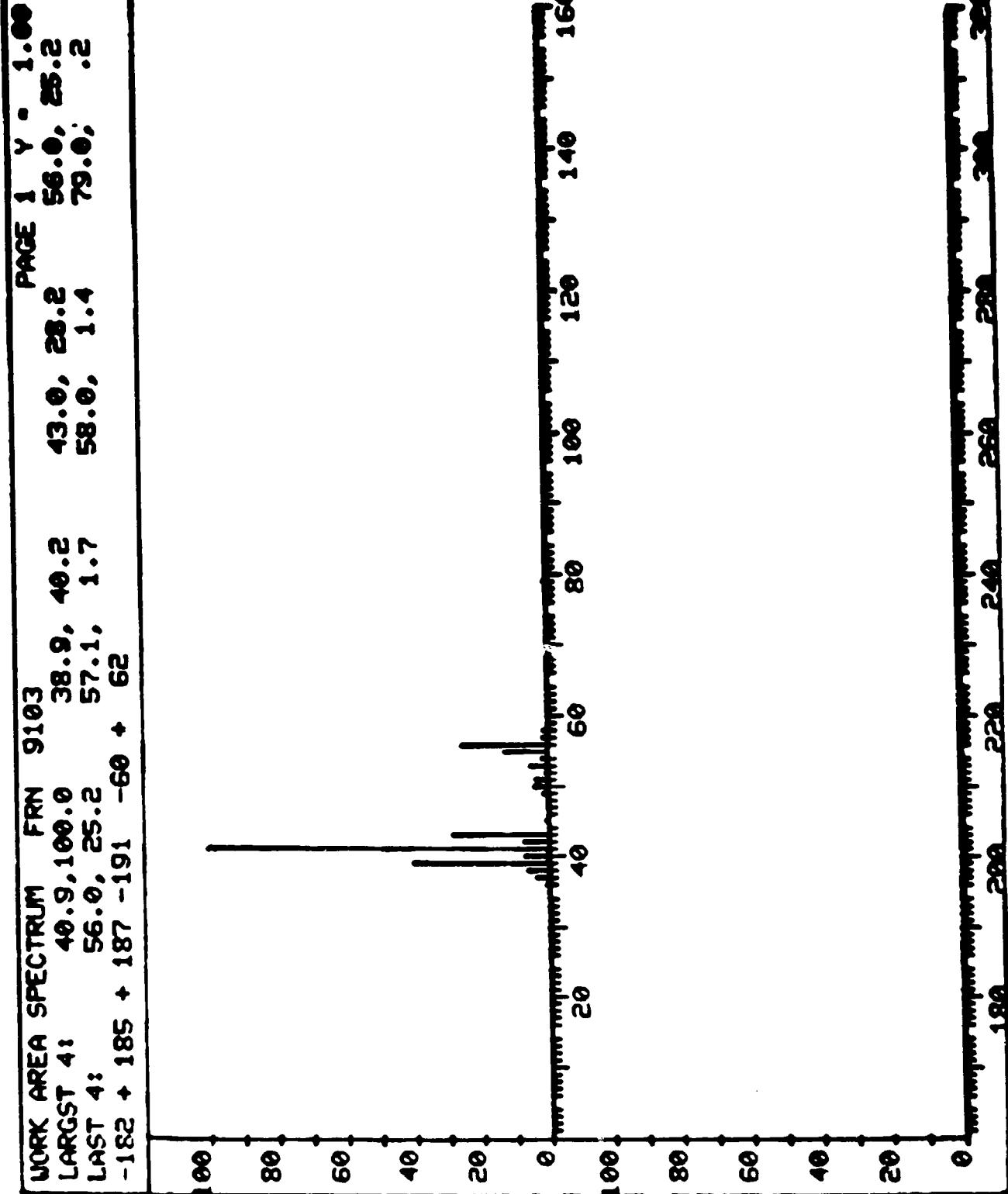
Figure A-2. Mass spectrum of isobutene reported in Table I.

WORK AREA SPECTRUM   FRN   9103   PAGE 1 Y = 1.00
LARGST 4:   41.0,100.0   38.9, 82.3   58.0, 30.8   43.0, 22.5
LAST 4:   57.0, 2.3   63.0, 1.9   65.0, 1.4   77.1, 1.4
-67 + 65
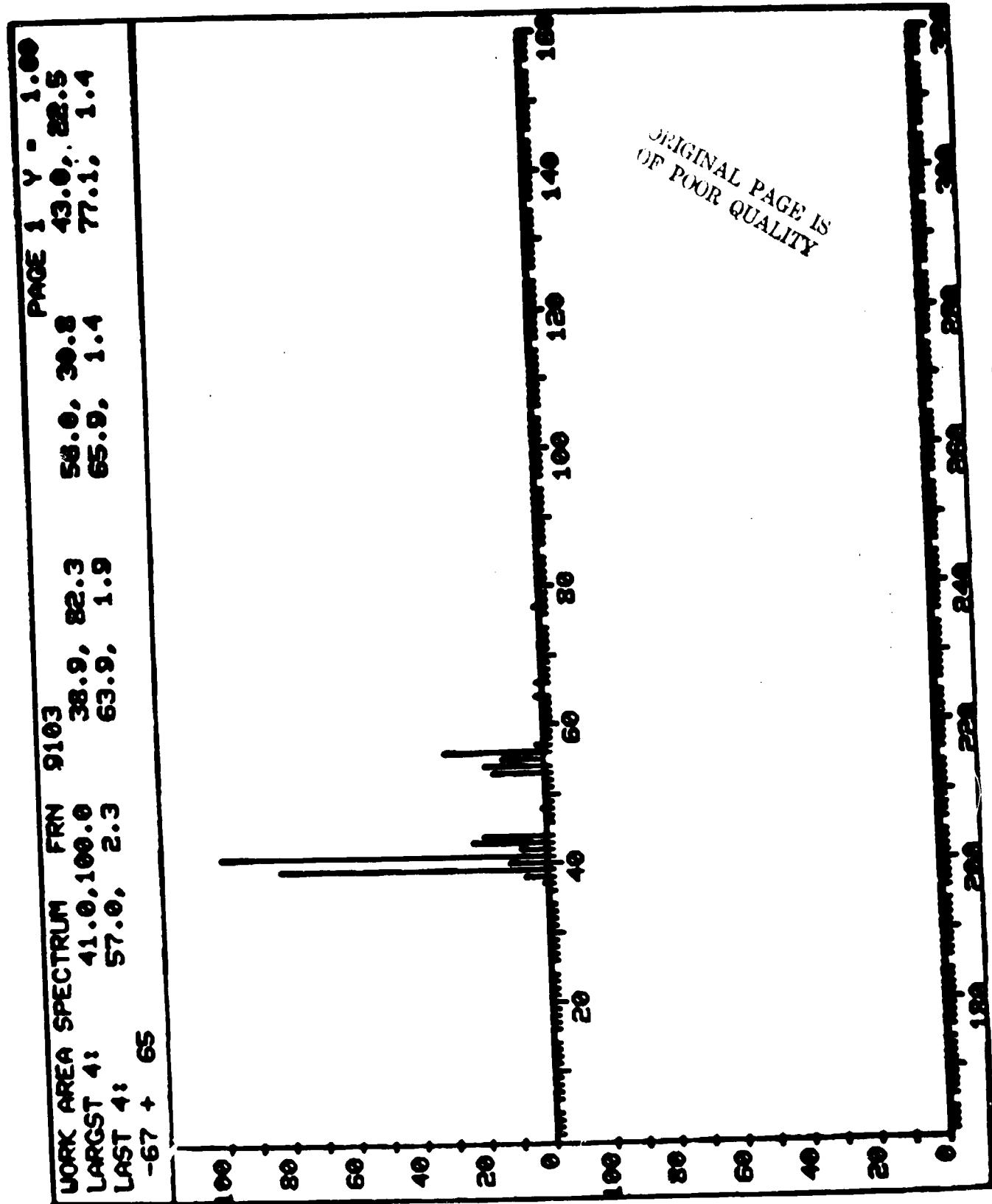
Figure A-3. Mass spectrum of 1,3-butadiene/butyne reported in Table 1.

Figure A-4. Mass spectrum of 1-buten-3-yne reported in Table I.
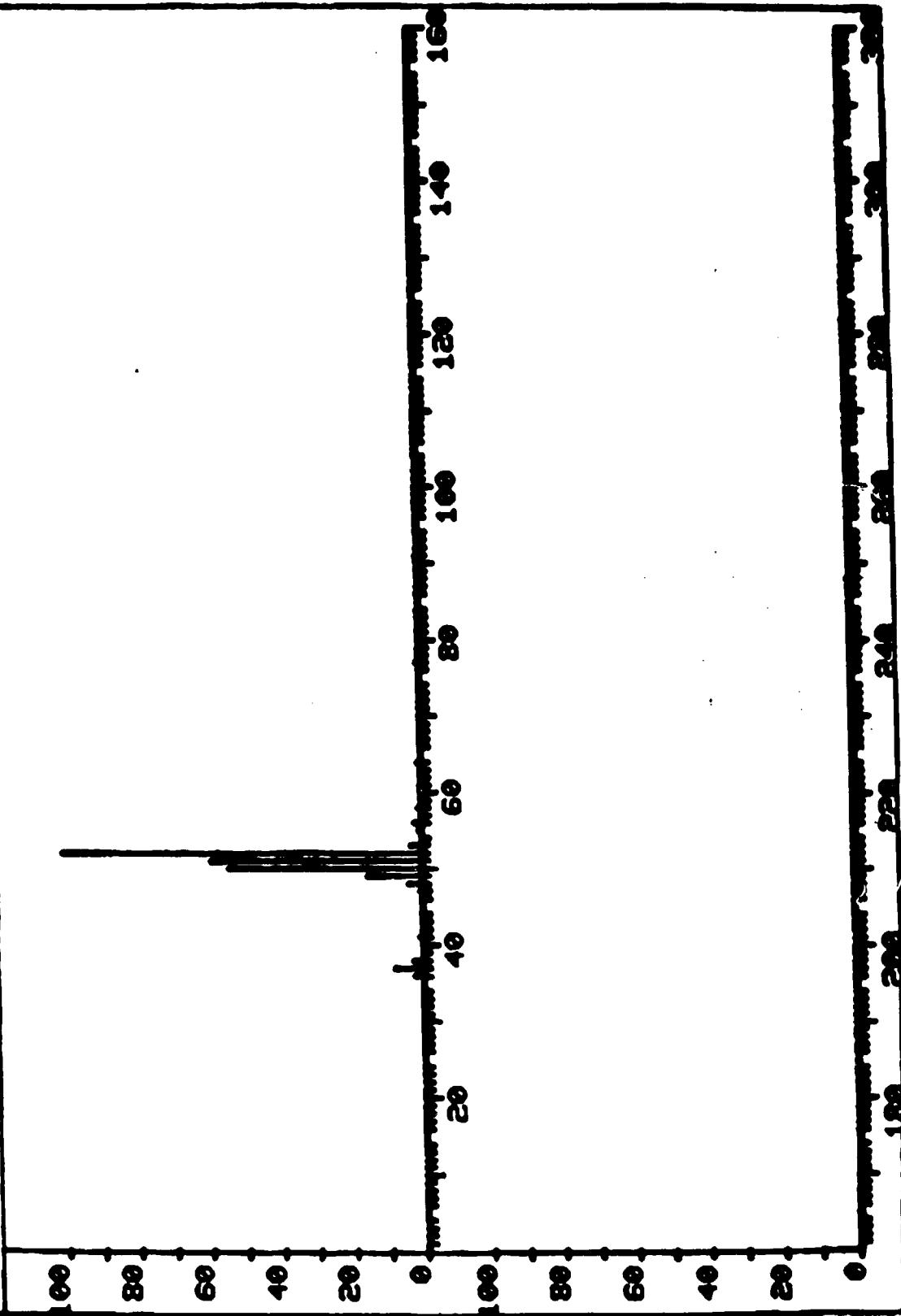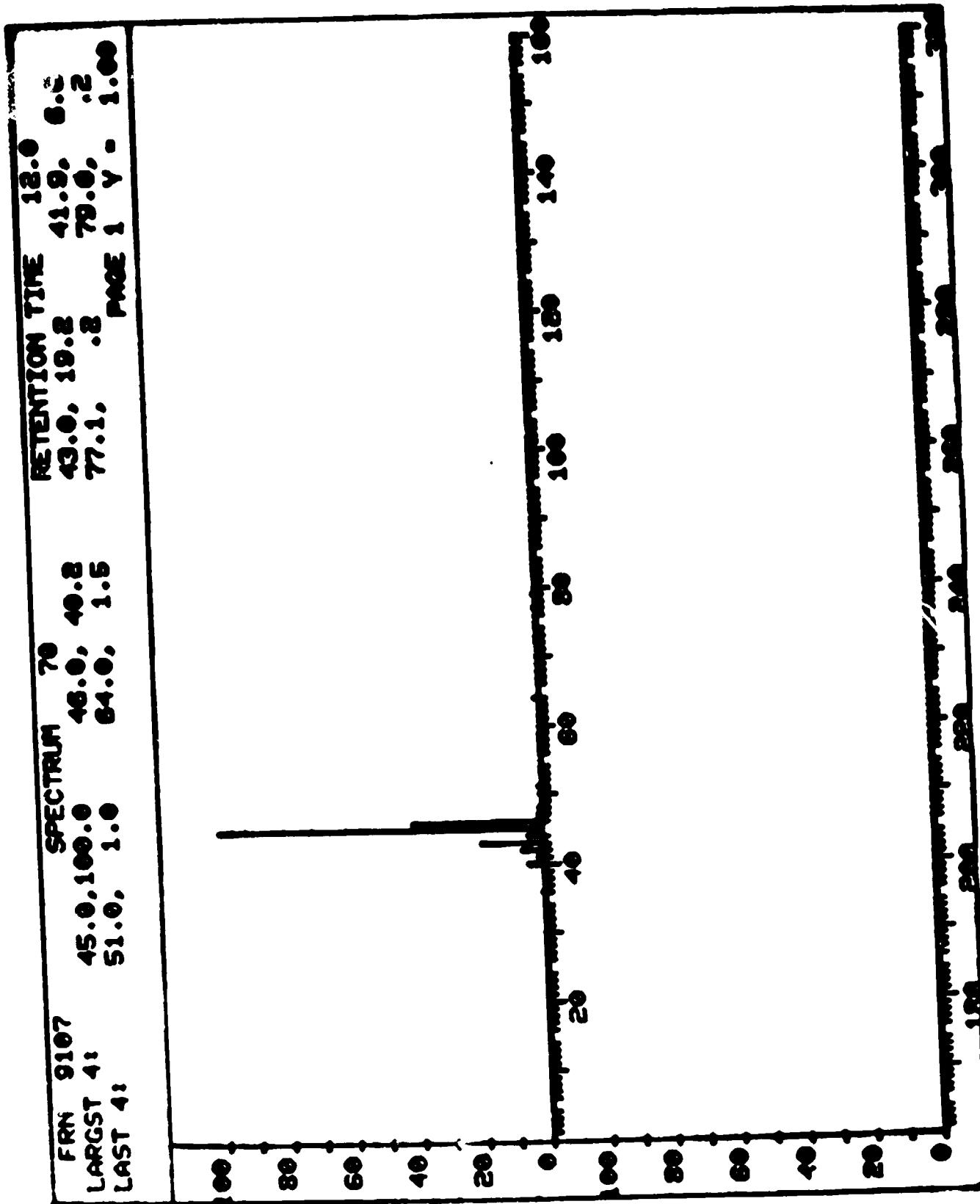
Figure A-5. Mass spectrum of ethanol reported in Tables I and II.
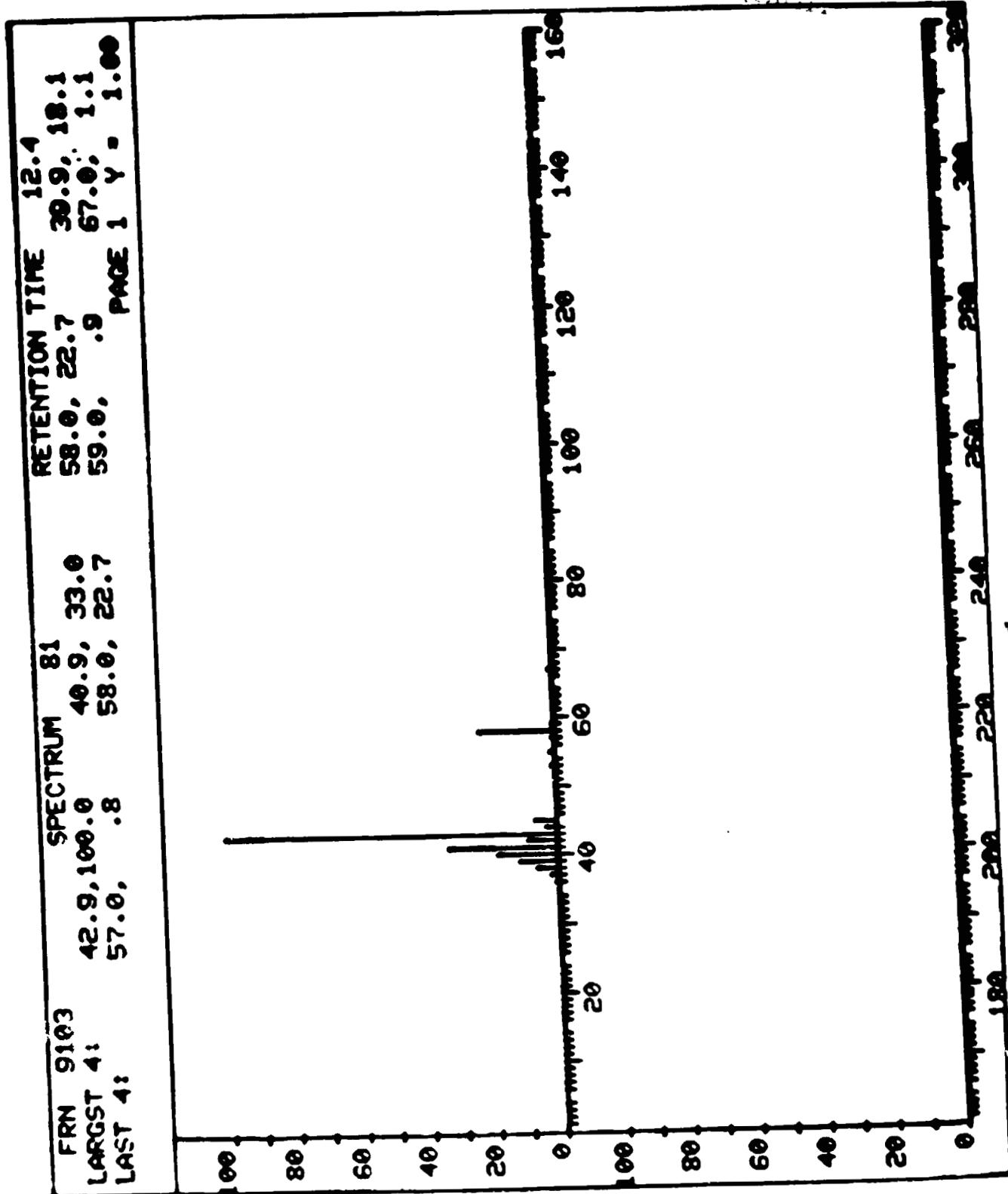
Figure A-6. Mass spectrum of acetone reported in Tables I and II.

Figure A-7. Mass spectrum of CS$_2$ reported in Tables I and II.
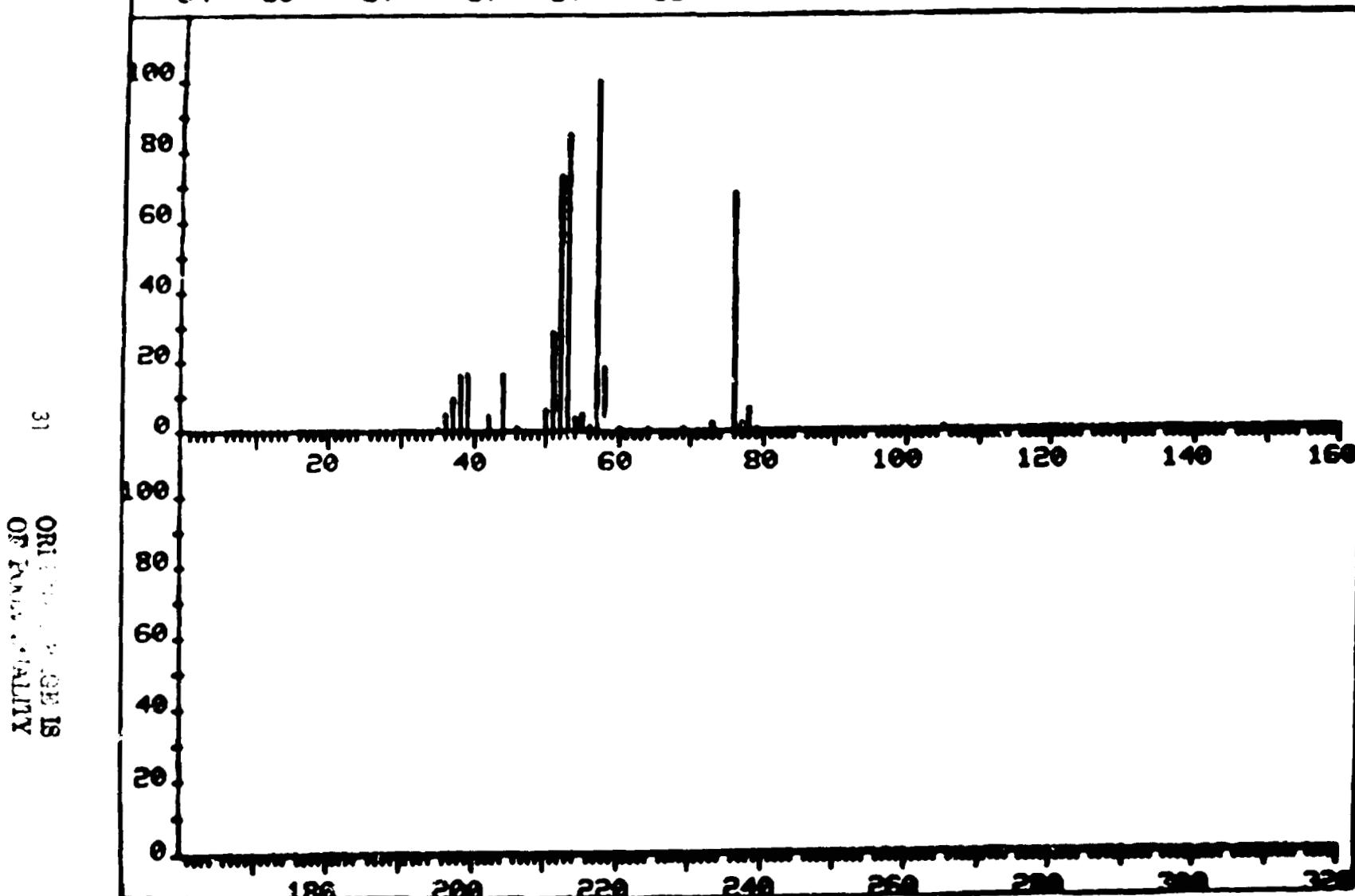
Figure A-8. Mass spectrum of propenenitrile reported in Tables I and II (note the presence of CS₂ and propene-1-ol).
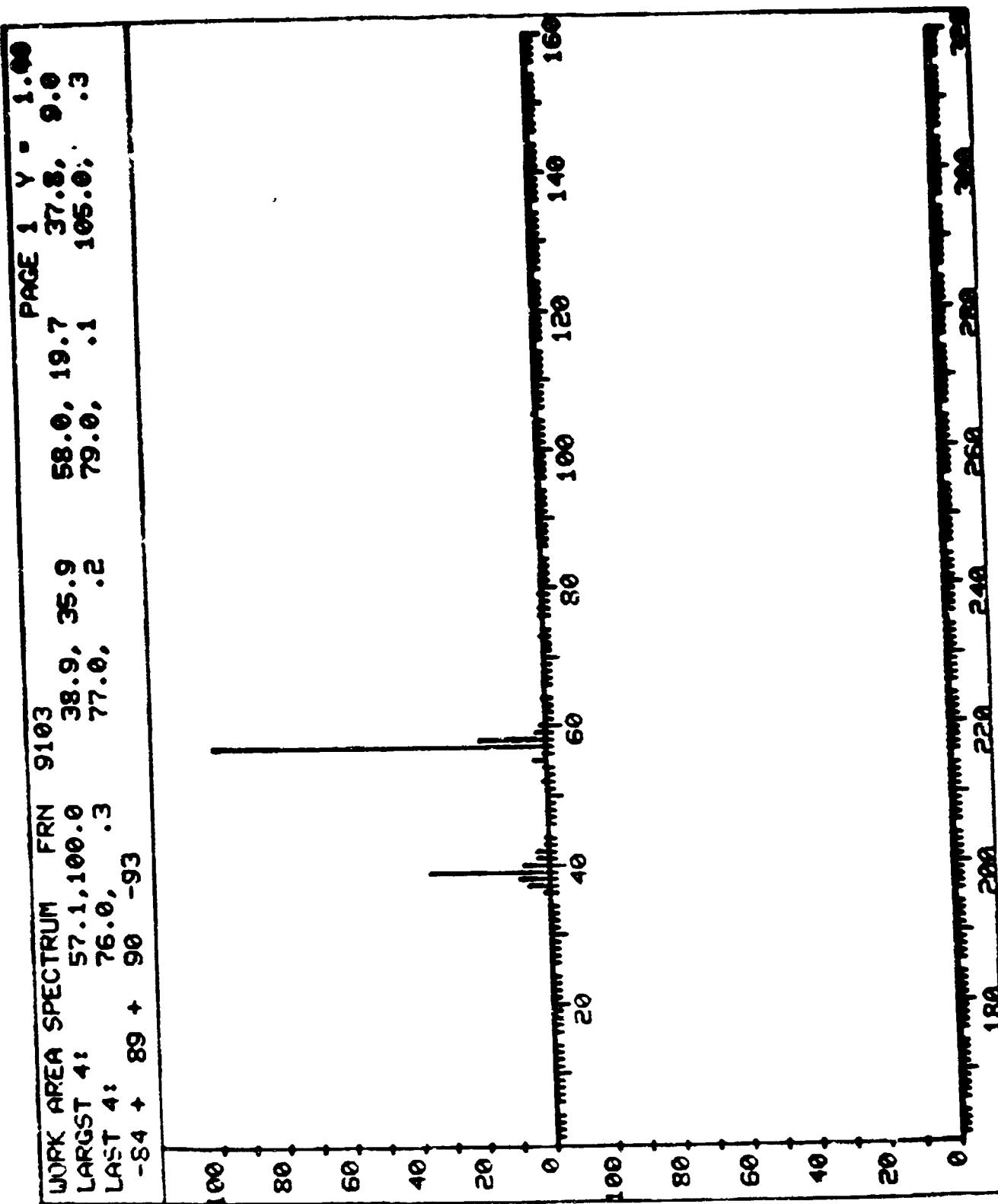
Figure A-9. Mass spectrum of propene-3-ol shown in Table 1.
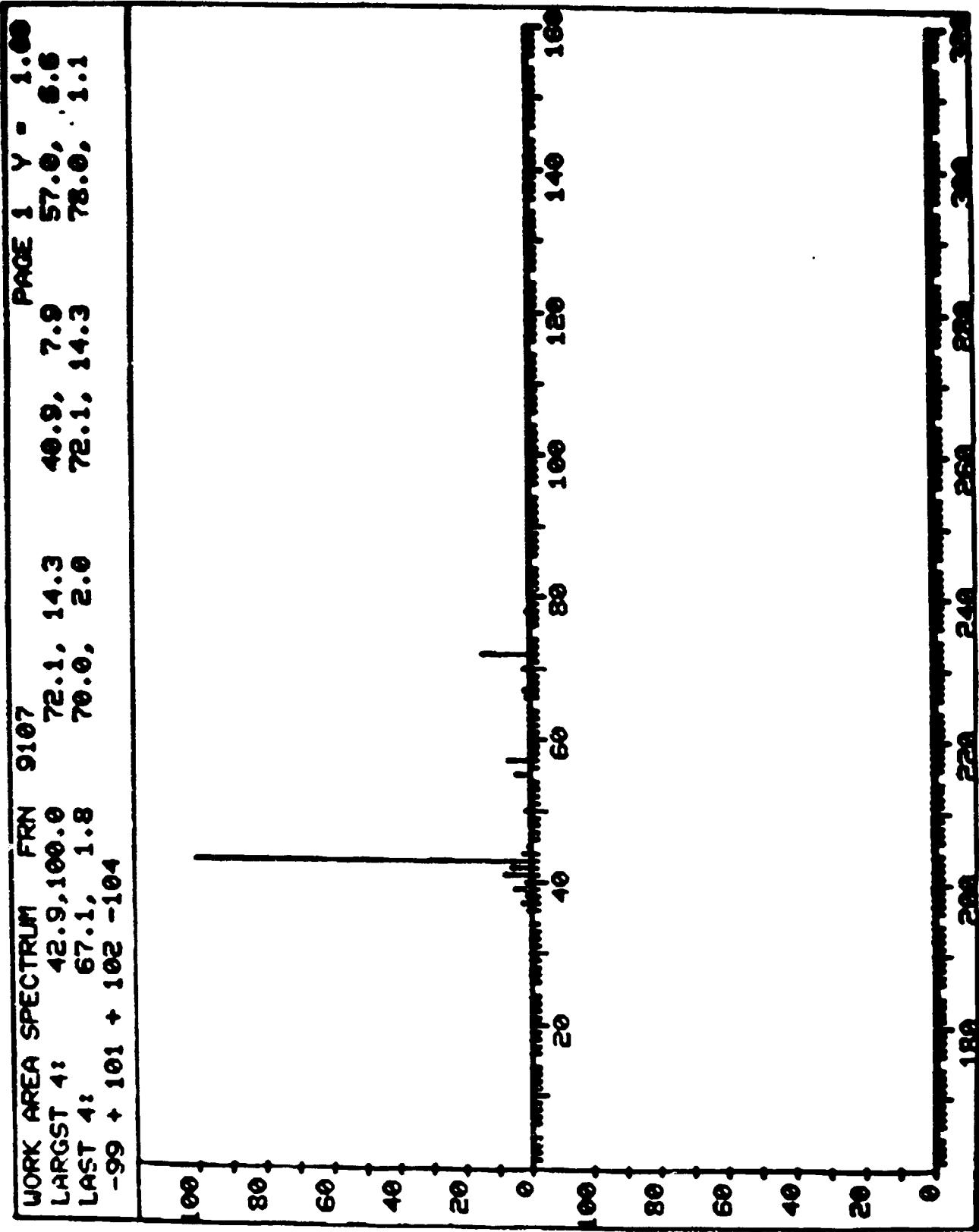
Figure A-10. Mass spectrum of methyl ethyl ketone shown in Tables I and II.

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FRN 9107   SPECTRUM 112   RETENTION TIME 17.3
LARGST 4:   78.1,100.0   51.0, 26.7   52.0, 26.6   50.0, 20.4
LAST 4:   78.1,100.0   79.1, 6.8   80.1, .2   104.1, .1
PAGE 1 Y = 1.00
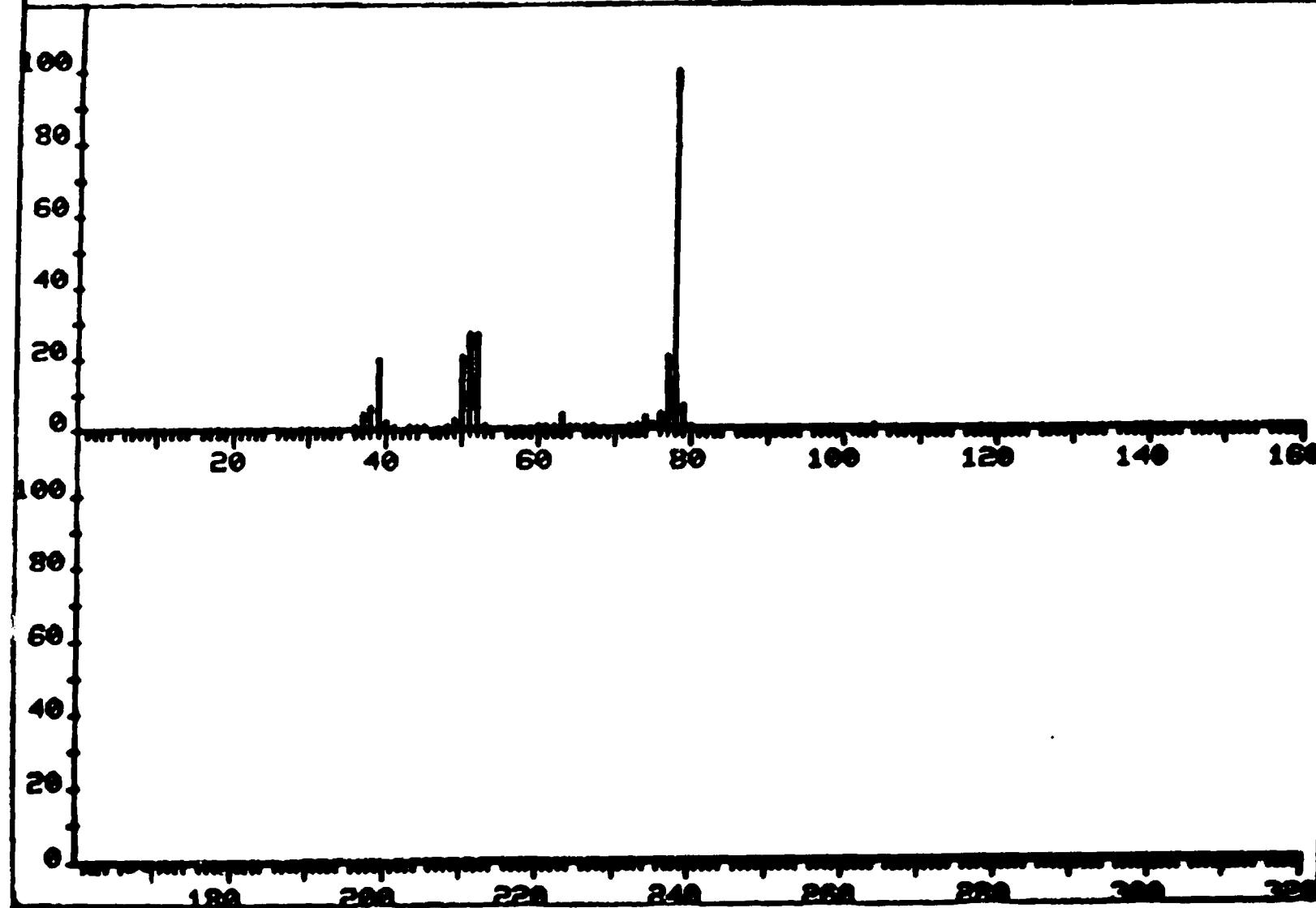
Figure A-11.   Mass spectrum of benzene shown in Tables I and II.
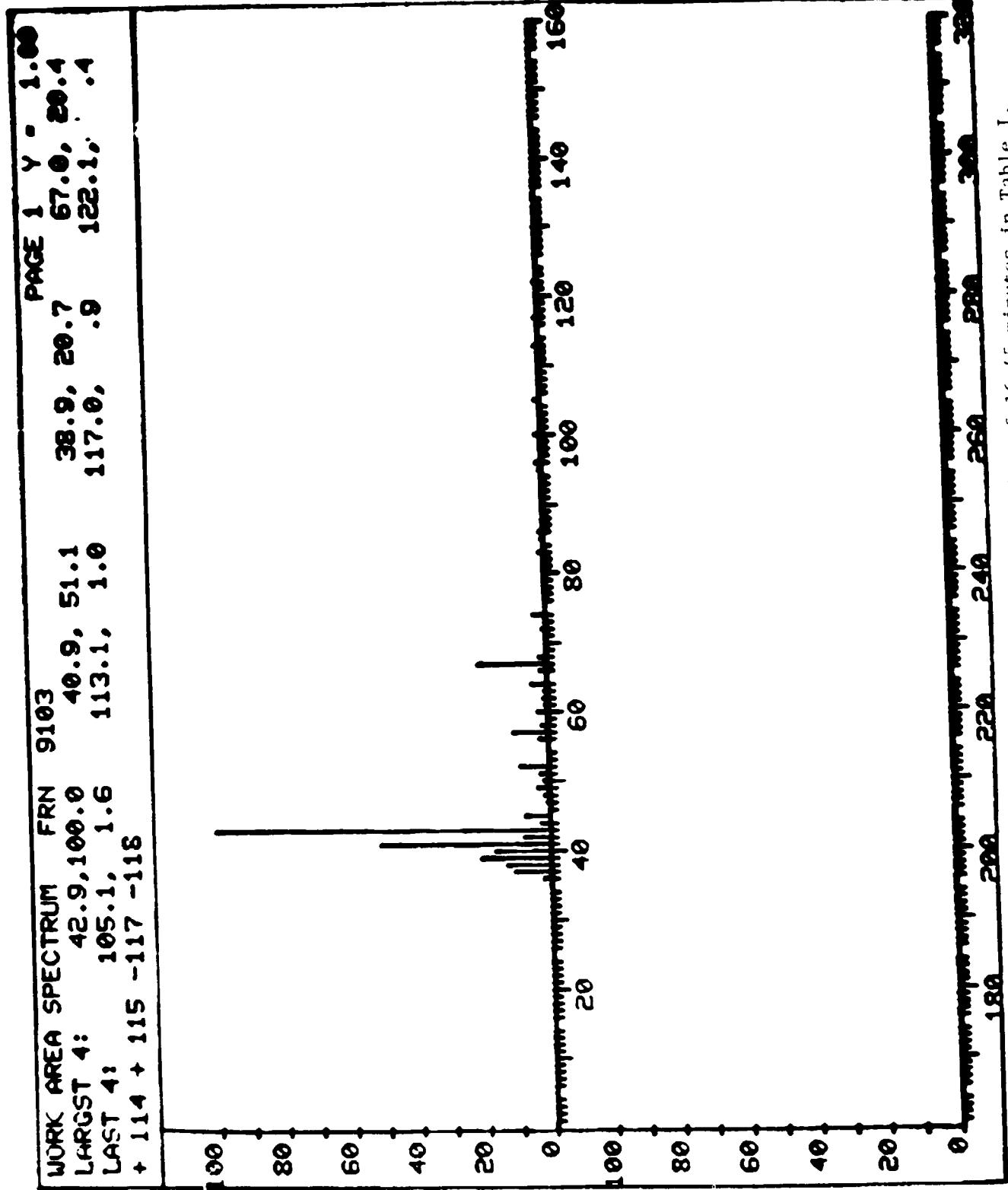
Figure A-12. Mass spectrum of compound with retention time of 16.45 minutes in Table I.
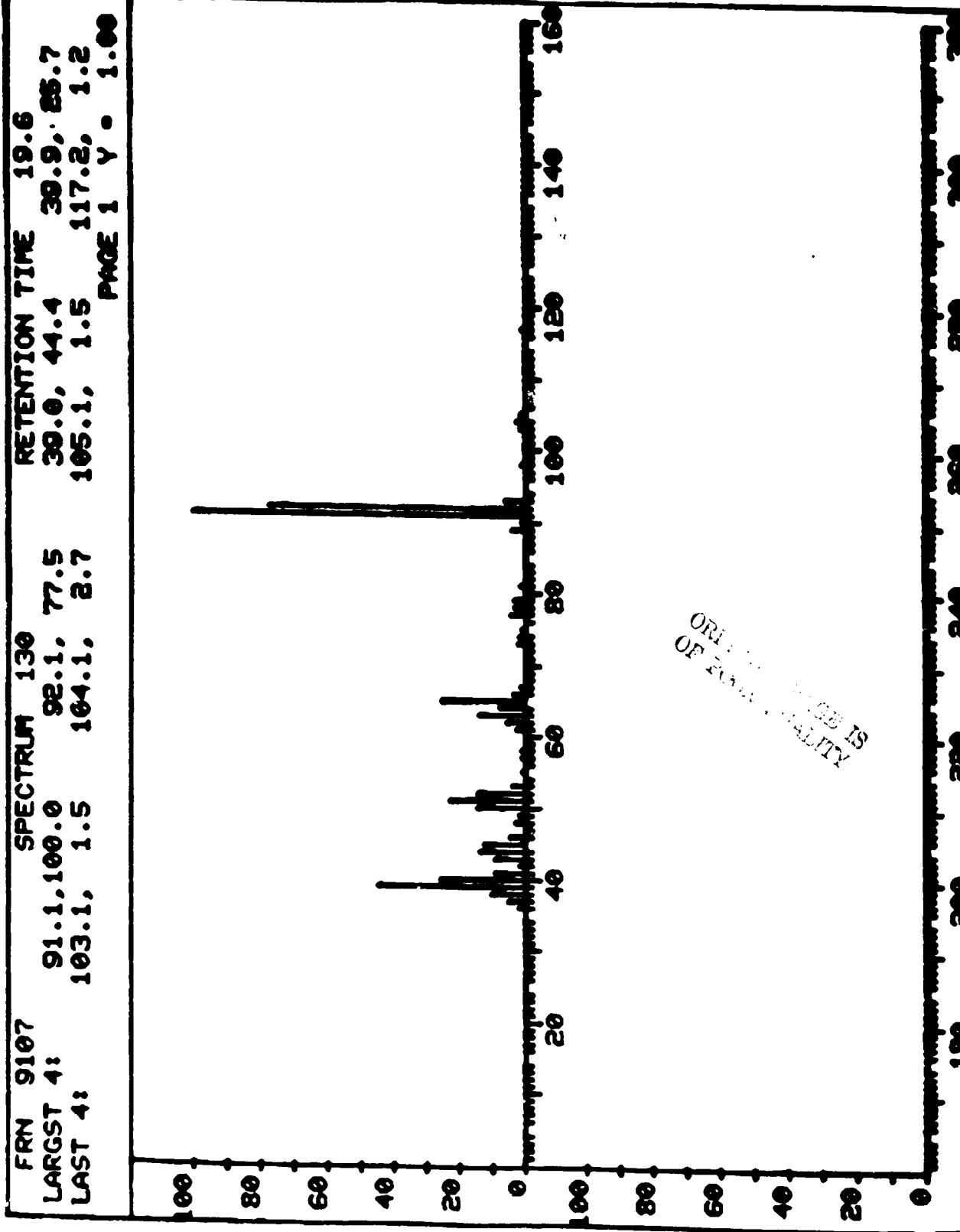
Figure A-13. Mass spectrum of toluene shown in Tables I and II.

Figure A-14. Mass spectrum of pyridine shown in Table I.

WORK AREA SPECTRUM   FRN   9109   PAGE 1 Y = 1.00
LARGST 4:   103.1,100.0   104.1, 94.4   59.1, 46.2   43.0, 42.2
LAST 4:   143.5, 4.0   158.3, 2.2   163.1, 3.6   199.0, 2.9
-137 + 141 + 142 -144
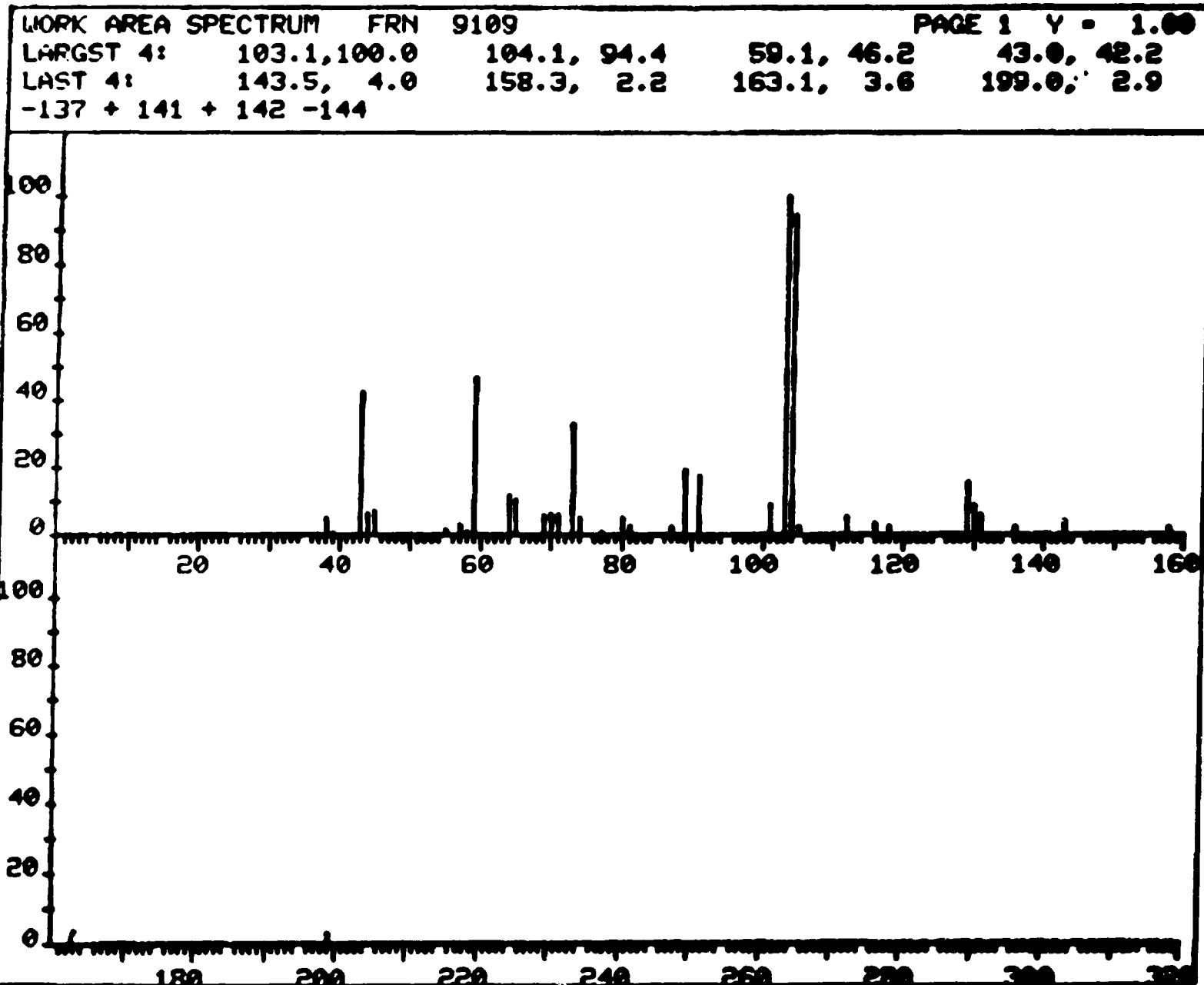
Figure A-15.   Mass spectrum of compound with retention time of 19.86 minutes with probable
molecular weight of 104.
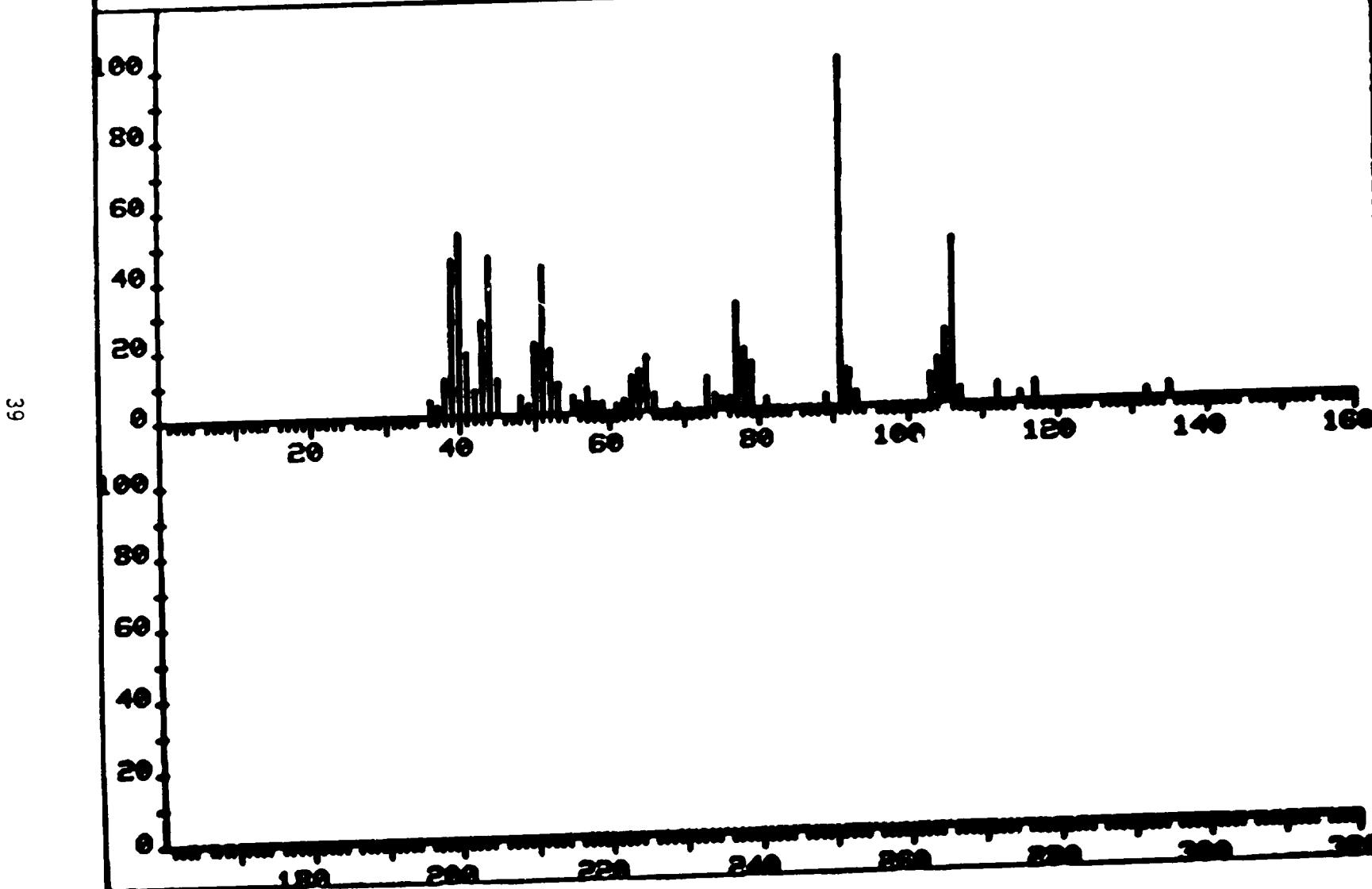
Figure A-16.   Mass spectrum of xylene shown in Tables I and II.
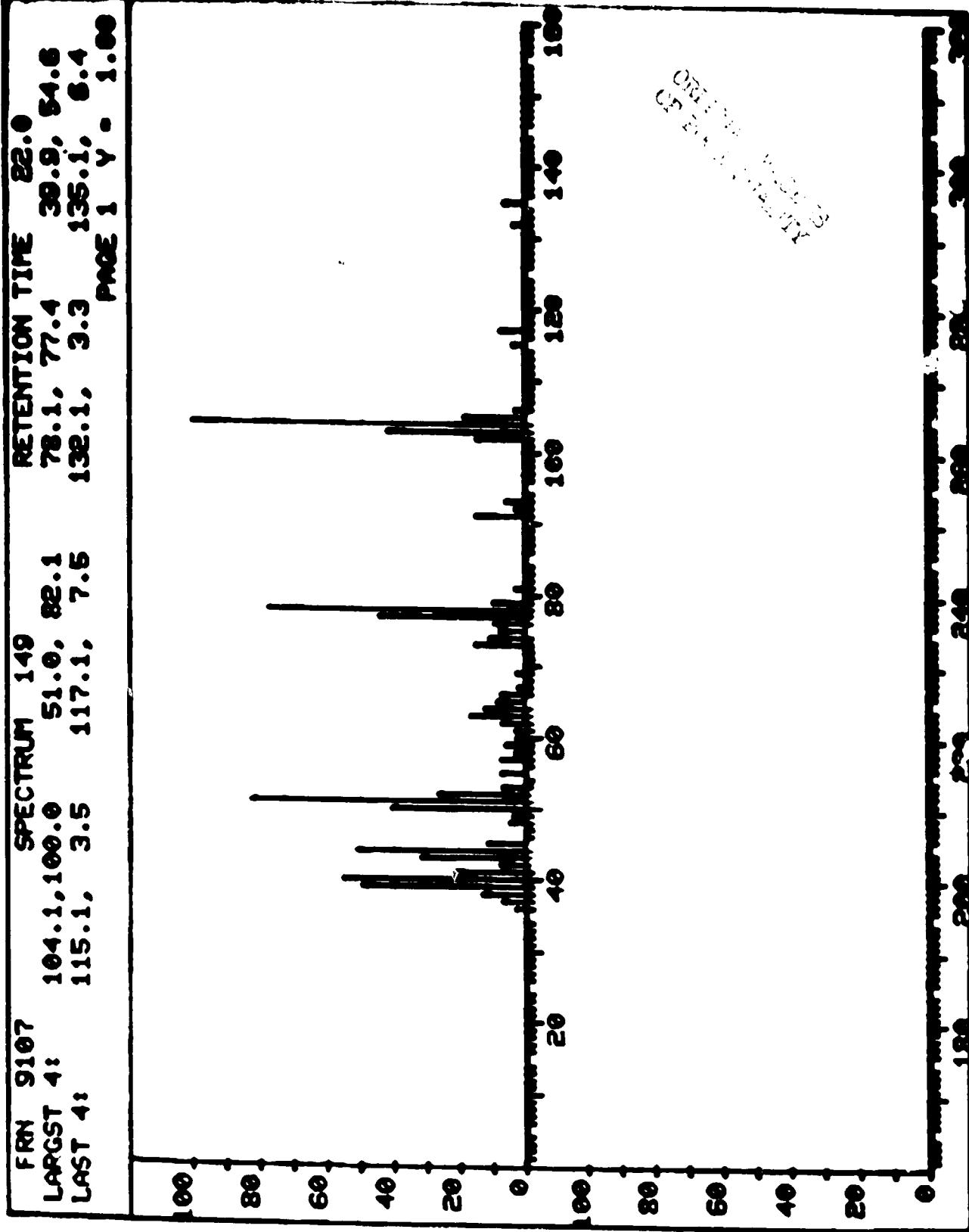
Figure A-17. Mass spectrum of styrene shown in Tables I and II.
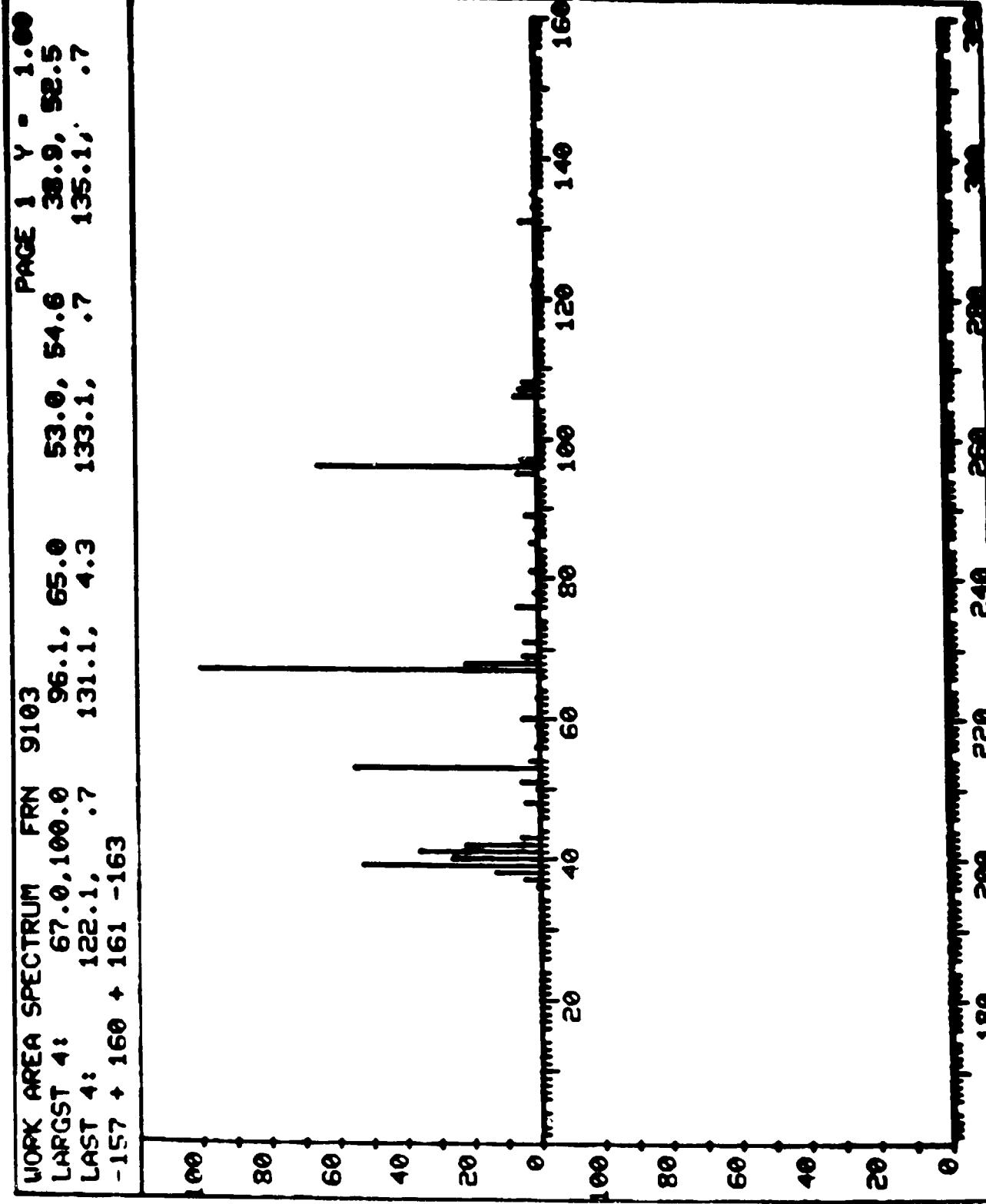
Figure A-18. Mass spectrum of compound with retention time of 22.36 minutes in Table I with probable molecular weight of 96.
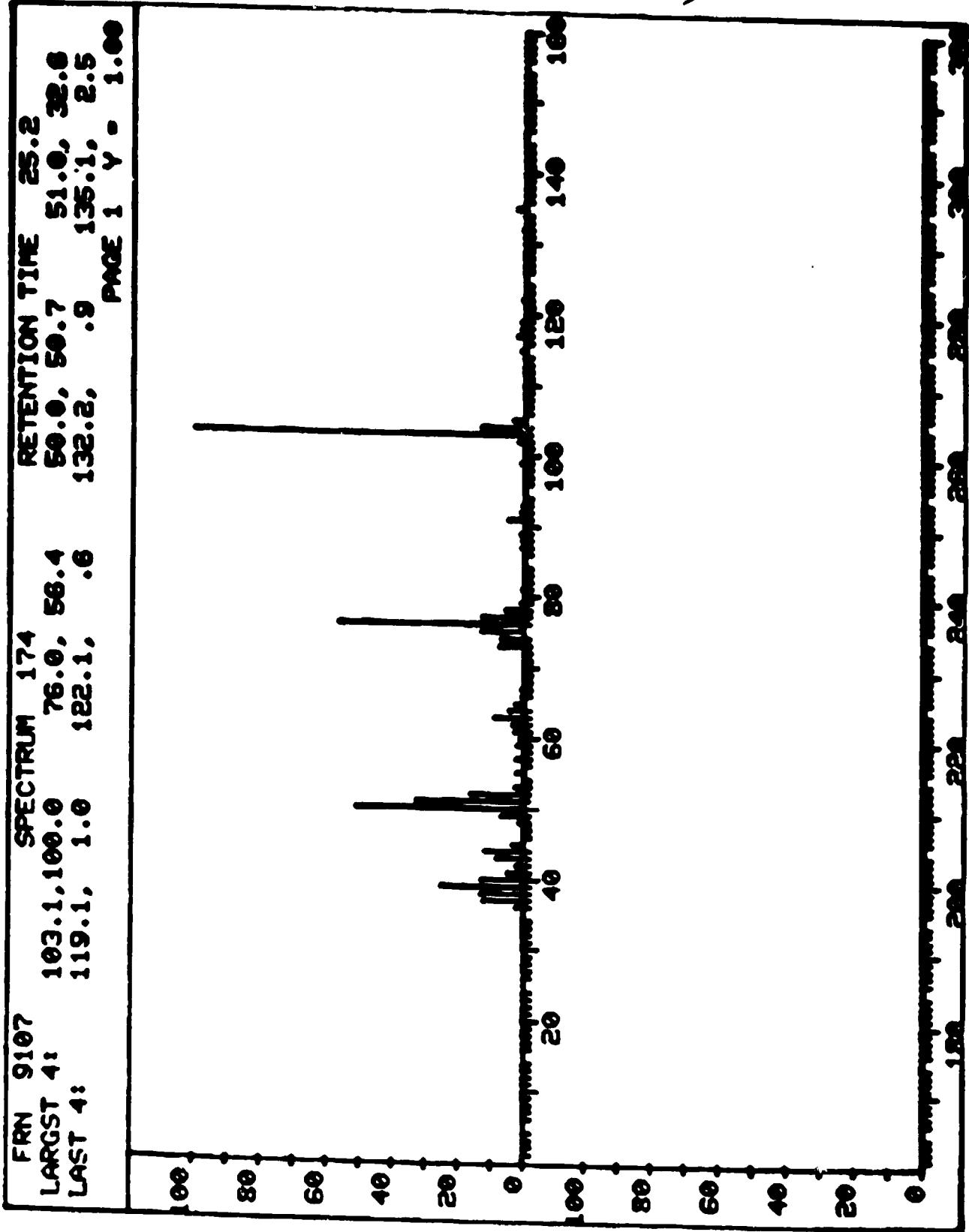
Figure A-19. Mass spectrum of benzonitrile shown in Tables I and II.
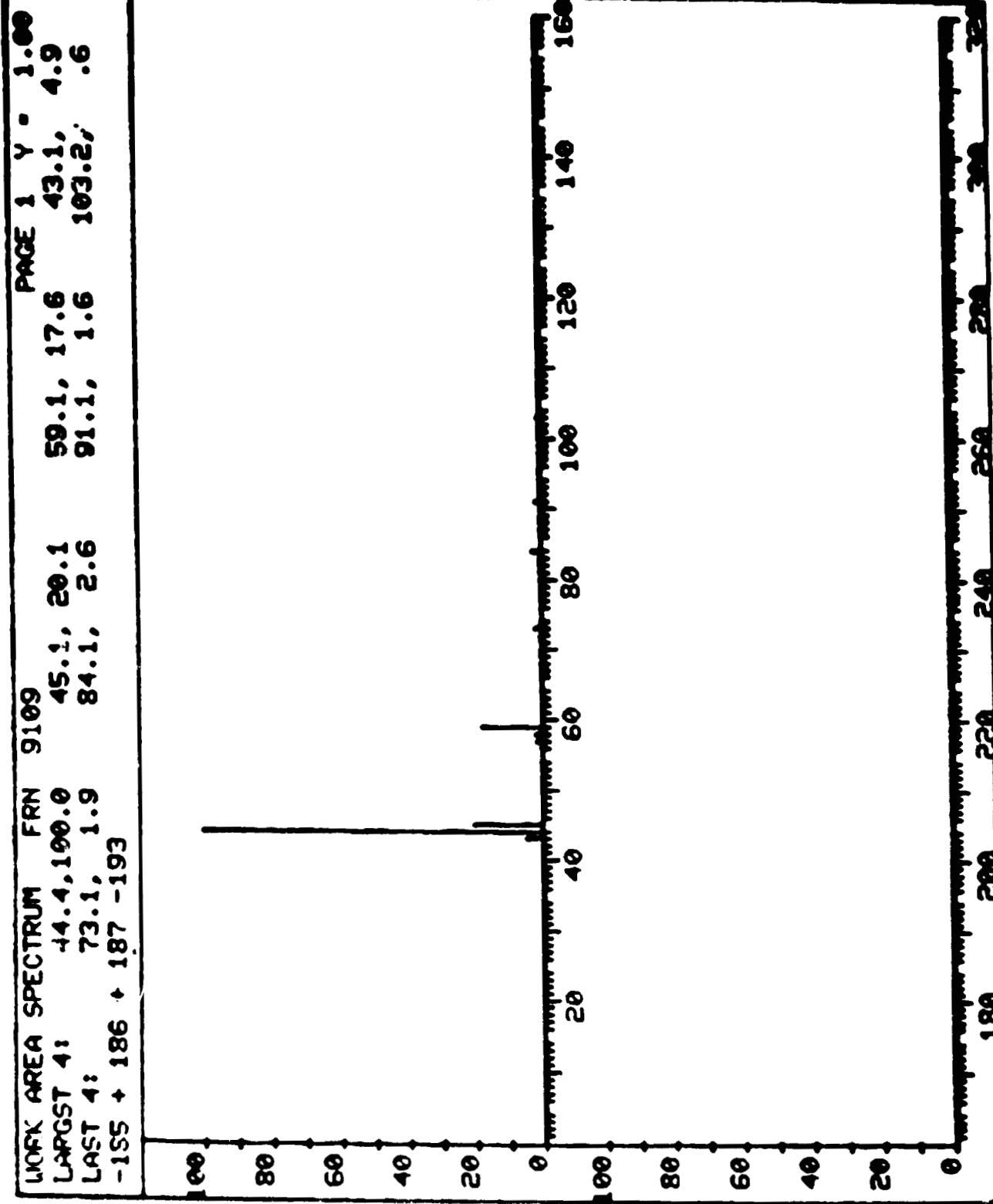
Figure A-20. Mass spectrum of compound with retention time of 25.61 minutes in Table I.
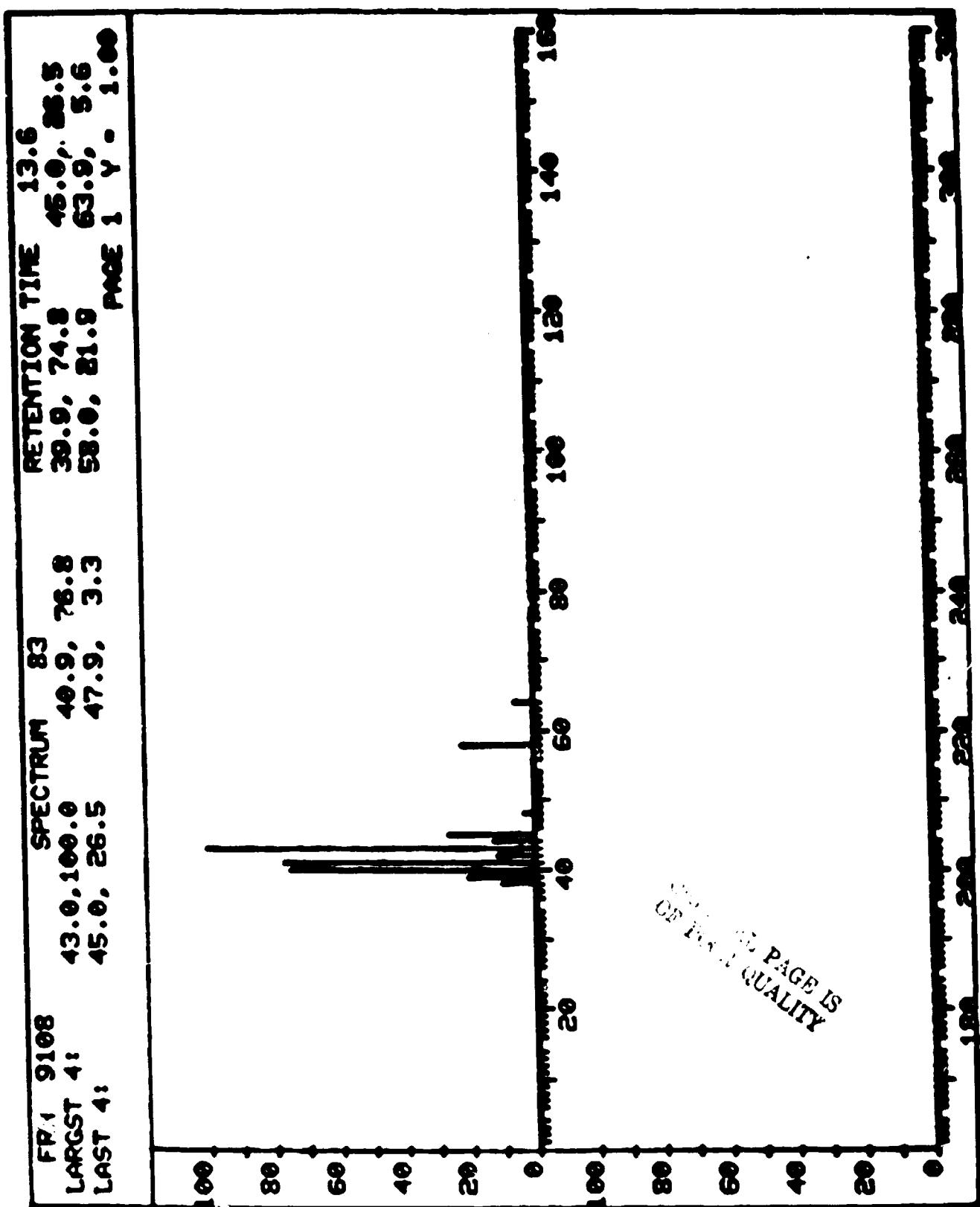
Figure A-21. Mass spectrum of isobutane/butane/propanol shown in Table 11.

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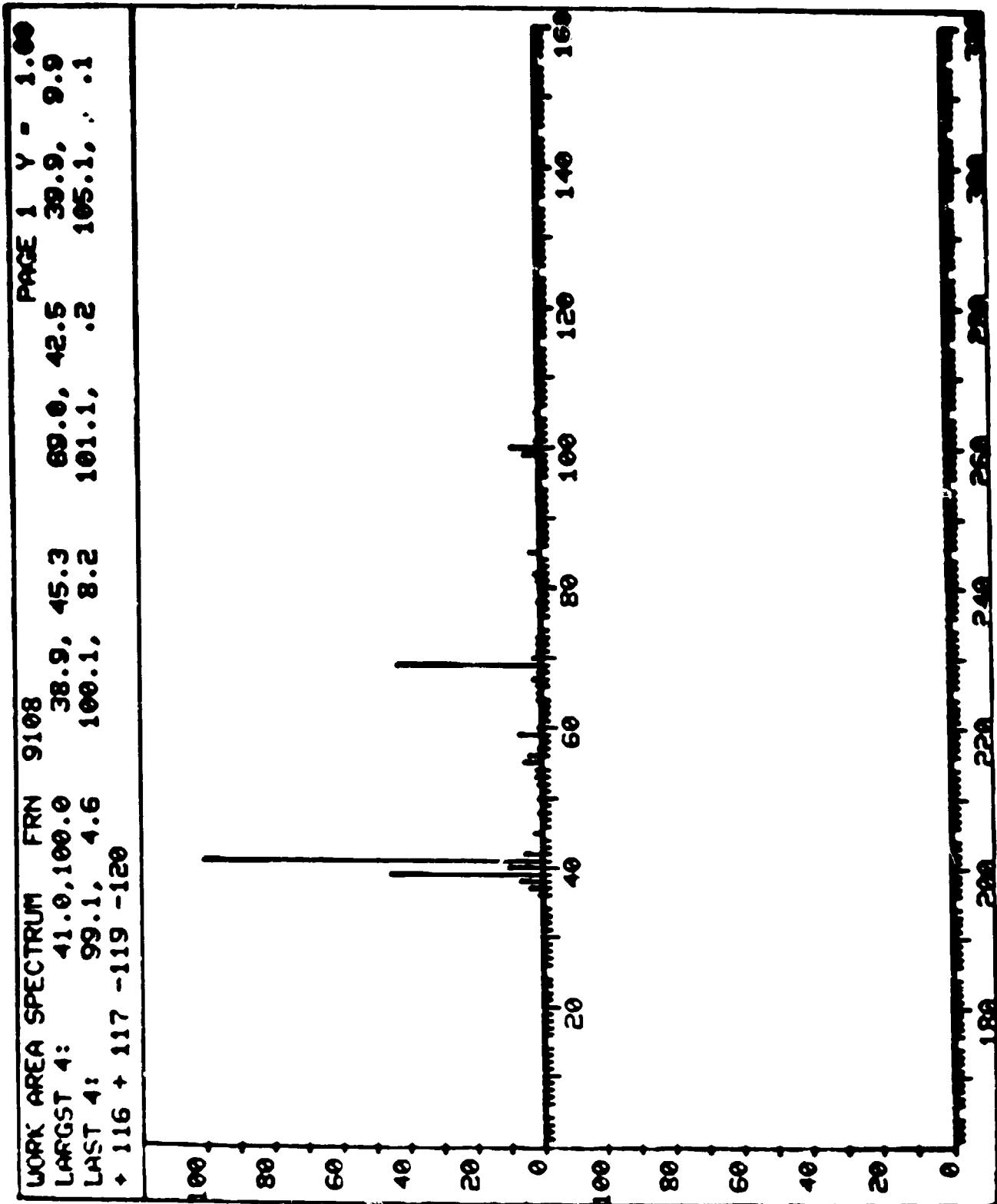
Figure A-22. Mass spectrum of compound with 17.82 minute retention time in Table II with probable molecular weight of 100.

WORK AREA SPECTRUM   FRN   9107   PAGE 1 Y = 1.00
LARGST 4:   40.9,100.0   38.9, 48.4   67.0, 45.2   36.9, 25.8
            67.0, 45.2   77.0, .6   78.1, 5.2   79.1, 8.4
LAST 4:
+ 157 + 158 + 159 -163 -175 -182 + 118 + 118 -118 + 119 -120 -121
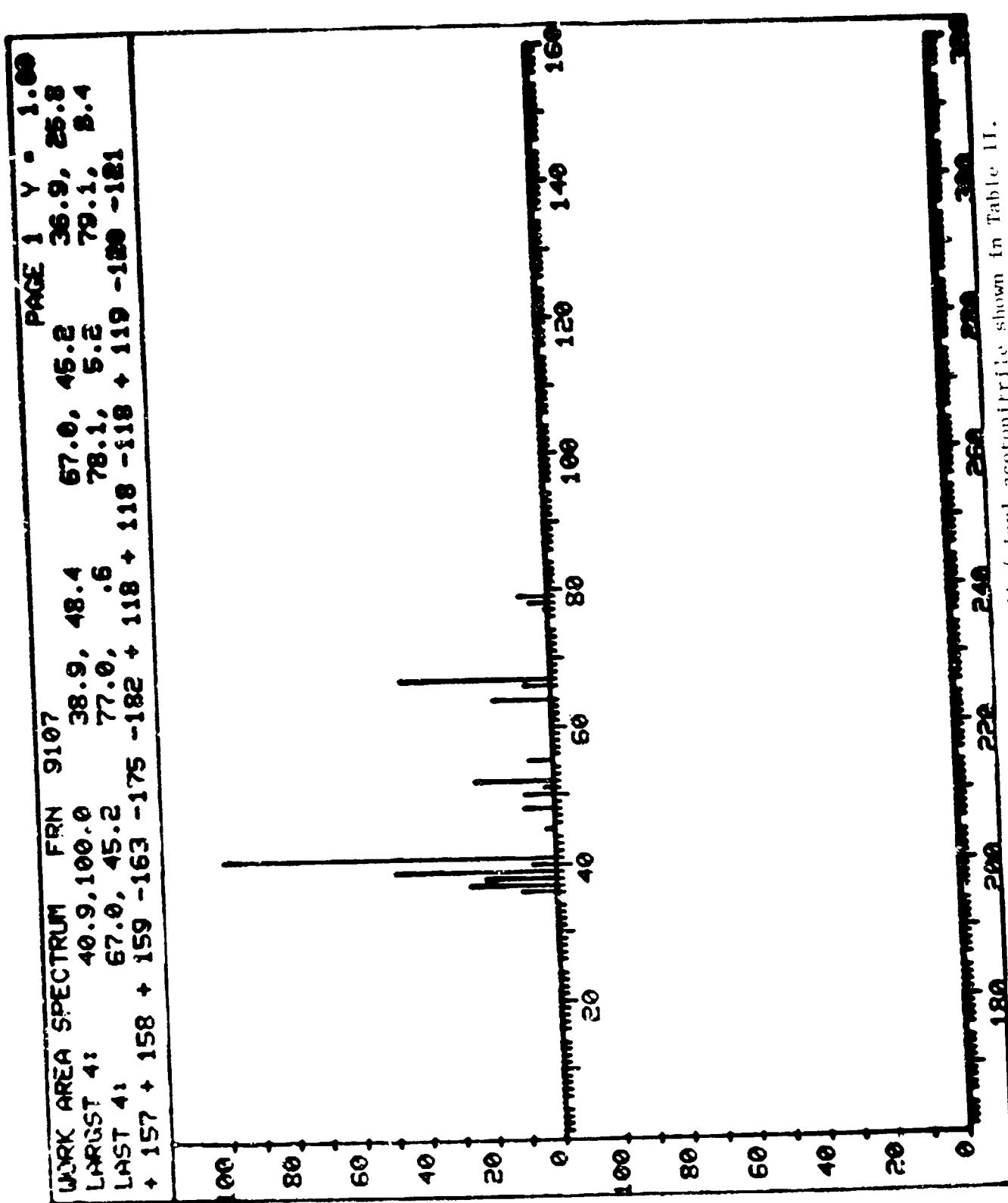
Figure A-23. Mass spectrum of methacrylonitrile/vinyl acetonitrile shown in Table II.
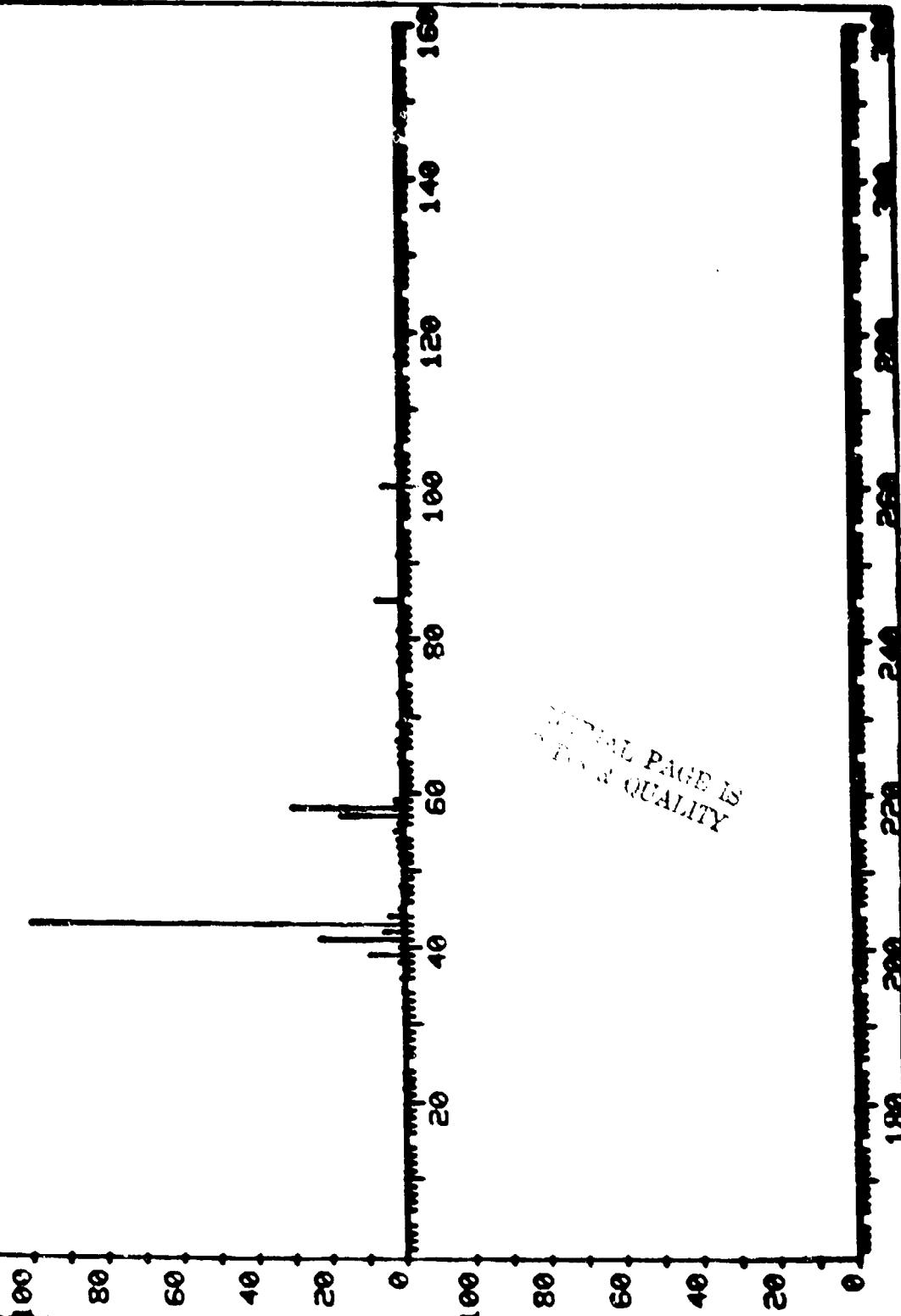
Figure A-24. Mass spectrum of 4-methyl-2-pentanone/2-hexane/methyl isobutyl ketone shown in Table II.
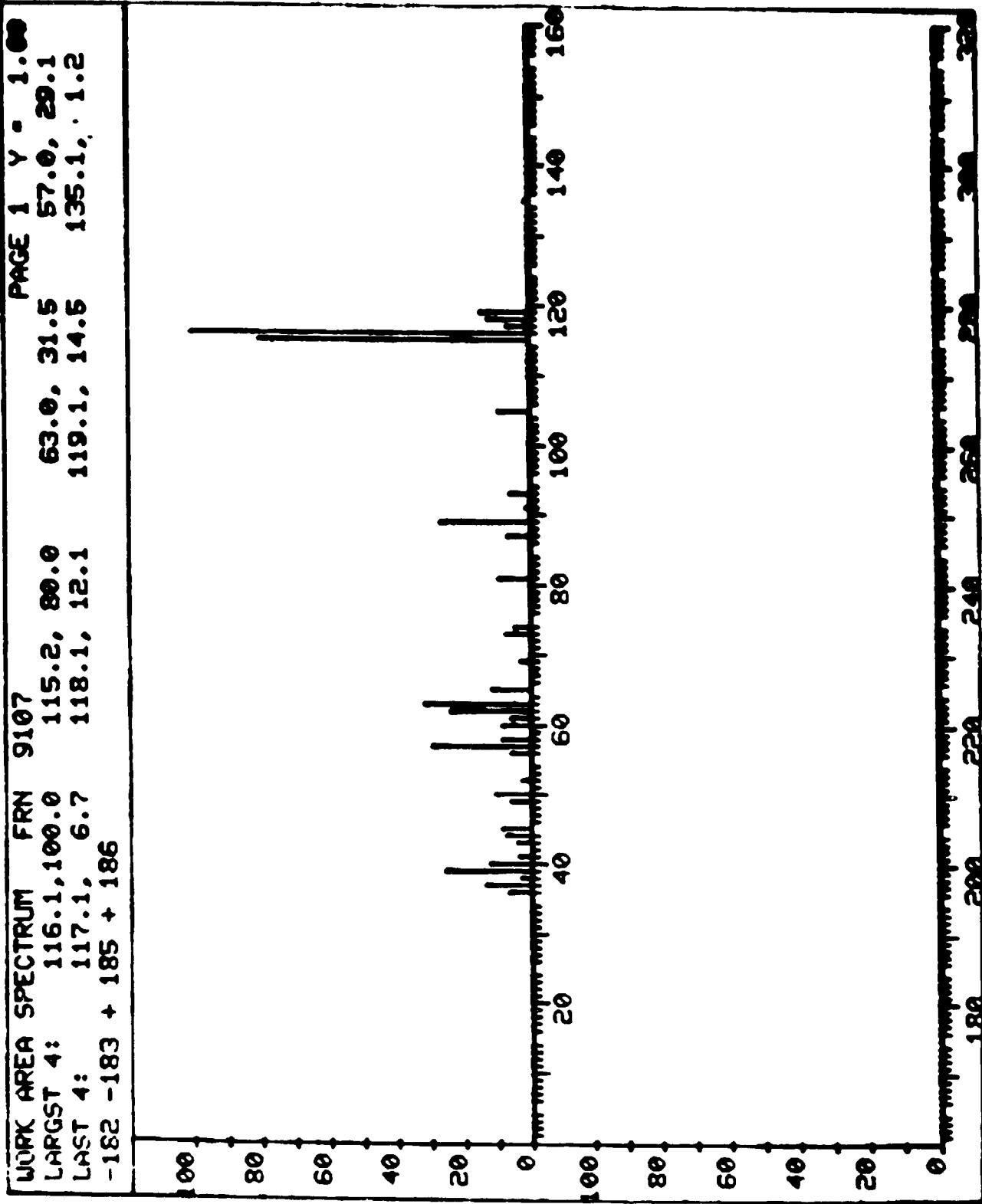
Figure A-25. Mass spectrum of compound with retention time of 26.7 minutes shown in Table II with probable molecular weight of 116.

WORK AREA SPECTRUM   FRM   9107   PAGE 1 Y = 1.00
LARGST 4:   44.0,100.0   42.0, 78.4   41.0, 51.3   99.1, 40.5
LAST 4:   118.1, .3   119.2, .7   131.2, .4   132.1, .8
+ 198 + 199 + 200 -218 -222 -224
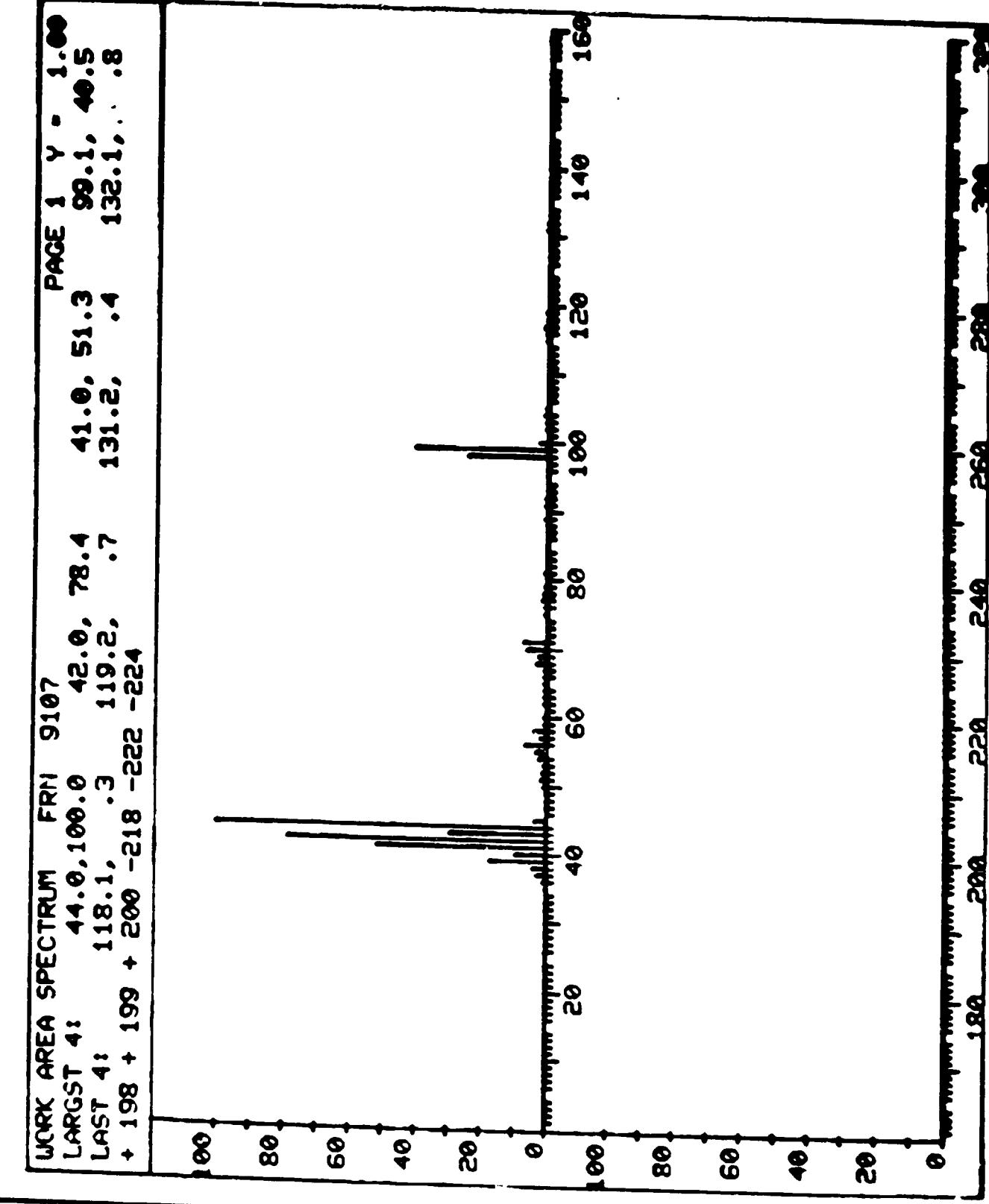
Figure A-26. Mass spectrum of N-methyl-2-pyrrolidone shown in Table II.

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Figure A-27. Mass spectrum of compound with 29.3 minute retention time in Table VI (note presence of N-methyl-2-pyrrolidone spectrum due to incomplete chromatographic resolution).

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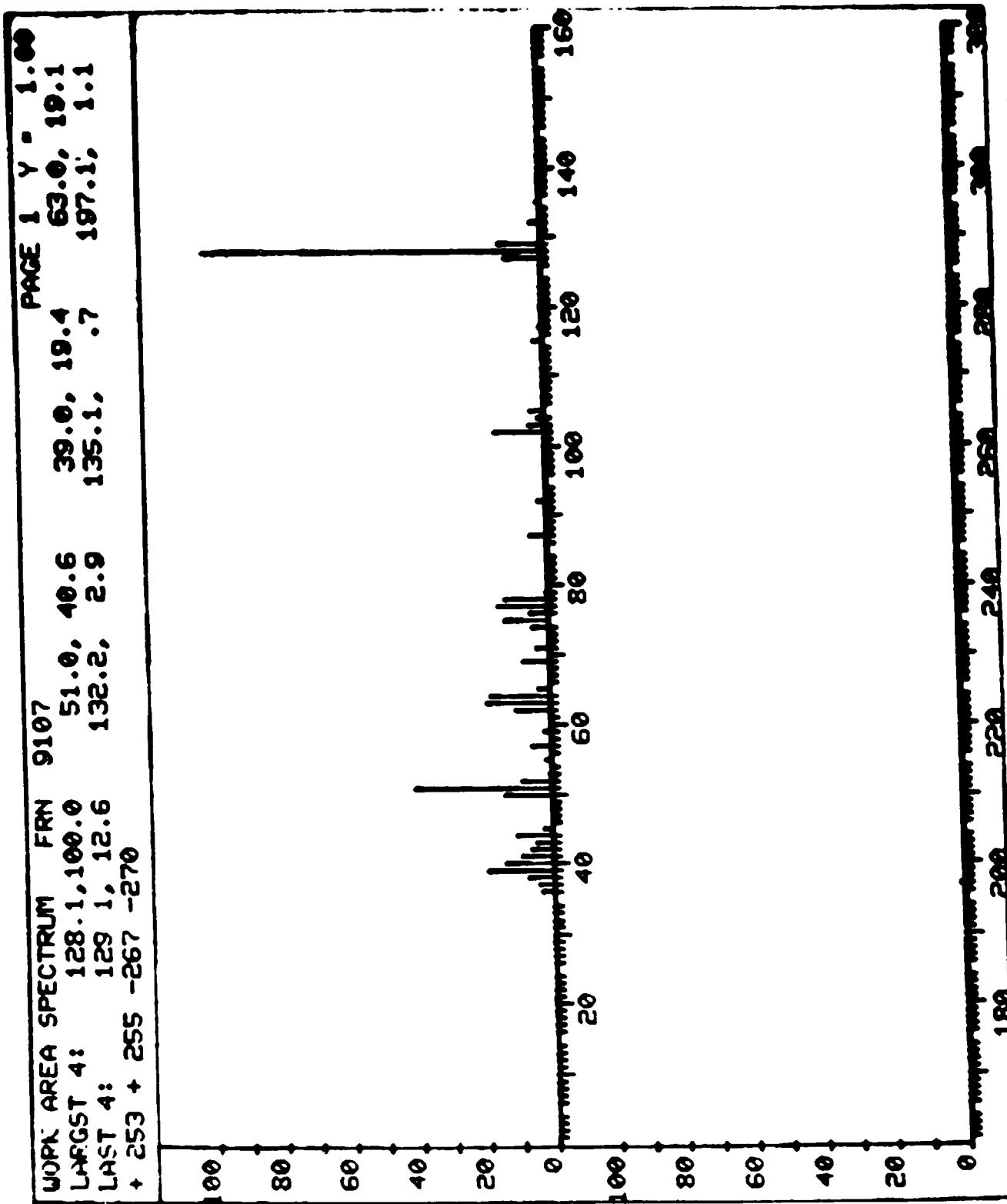
Figure A-28. Mass spectrum of compound with 35.31 minute retention time (probable molecular weight 128).

SECTION III

Oxygen Extinguishment Indices of Glass Laminates of an Epoxy Resin

MY-720 and a Bismaleimide Resin M-751 Under Simultaneous

Exposure to Radiant Heat

R. W. Arhart
T. L. Blank

Section III

Oxygen Extinguishment Indices of Glass Laminates of an Epoxy Resin MY-720 and a Bismaleimide Resin M-751 Under Simultaneous Exposure to Radiant Heat

Introduction

Glass laminates of epoxy resins would not be expected to be the primary origin of a fire because of their relatively high level of flame retardance. Their good flame retardant characteristics are the result of the low flammability of the resin and the diluent effect of the glass substrate. The most likely fire scenario for flat glass laminates is one in which the laminate is subjected to radiant energy from a fire which is remote to the laminate. The propensity of the laminate to become involved in the fire is probably most dependent on the radiant energy impinging upon the sample and the concentration of oxygen in the atmosphere around the sample. Therefore, a proper and realistic test procedure for these materials would involve the observation of a chosen flammability characteristic of the laminate as a function of radiant energy impinging the surface and oxygen concentration of the atmosphere around the sample.

Such a flammability test has been developed by A. Tewarson [1]. In Tewarson's device, a sample in a large glass tube is displayed horizontally to radiant energy. The oxygen concentration of the atmosphere, which enters the bottom of the tube and flows past the sample, is regulated. After igniting the sample, Tewarson measured parameters such as rate of mass loss, rate of heat loss, smoke evolution and

oxygen extinguishment index. For the work described in this report a device similar to Tewarson's, but of more limited scope was constructed.

The object of this work was to measure the oxygen extinguishment index of two glass laminates of epoxy resin and bismaleimide resin. The oxygen extinguishment index (OEI) is the minimum concentration of oxygen which will maintain flaming oxidation of a sample which is exposed simultaneously to a given flux of radiant energy. The term oxygen extinguishment index (OEI) is used instead of limiting oxygen index (LOI) to avoid confusion with the rigidly defined ASTM test procedure for the determination of the latter. In the test procedure used in this work a vertically displayed laminate was subjected to radiant energy and was ignited with a pilot flame. The oxygen concentration of the atmosphere flowing around the sample was then decreased until flaming oxidation ceased. The oxygen concentration at extinguishment is defined as the oxygen extinguishment index (OEI). A vertical display of the sample was chosen for two reasons. First, it enabled closer placement of the radiant energy source to the sample, thereby allowing higher heat fluxes. Second, a vertical display is probably the most common arrangement the laminates will have in actual use. Thus, the combination of vertical display of sample and environment of radiant energy and variable oxygen concentration was intended to furnish a realistic assessment of the tendency of flat glass laminates to become active components of a fire. Furthermore, the authors believe that the test procedure presented in this report when used in combination with limiting oxygen index values of neat resin, toxicological evaluation of

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combustion products, and chemical analysis of combustion products results in a sophisticated, realistic assessment of the flammability hazards of glass laminates.

Experimental

Apparatus

A photograph of the instrument used for determination of the oxygen extinguishment index is shown in Figure 1. A labeled schematic of the instrument is shown in Figure 2. In the following discussion the numbers is parenthesis refer to the appropriate items in Figure 2.

Oxygen, nitrogen, and air were introduced to the mixing chamber (1) via individual flowmeters (2). After exiting the mixing chamber the atmosphere was introduced at the bottom of the glass cylinder through three symmetrically positioned inlet ports (3). To disperse the gas and ensure an even nonturbulent upward flow, the bottom of the glass cylinder (4) contained a six inch high stainless steel cylinder (5) which was filled with glass spheres of diameter 1 cm. The diameter of the steel cylinder (O.D., 6 7/16") was nearly equal to that of the glass cylinder (ID, 6 3/4"). The small dead space (6) between the steel cylinder and glass cylinder was filled with asbestos matting and glass wool. The flow rate of atmosphere through the glass cylinder was a constant 1 ℓ/sec for all experiments. That flow rate translated to 4.3 cm/sec vertical velocity in the glass cylinder.

The samples consisted of squares of material, three inches by three inches. The polymethyl methacrylate (PMMA) specimens were .250

inches thick. The glass laminates were all .125 ± .010 inches thick. Samples were contained in NBS-Aminco Smoke Density sample holders (7). The specimens were backed with one layer of aluminum foil and a 1/2 inch thick layer of transite. The exposed area was a square, 2 3/4 X 2 3/4 inches. Surfaces were exposed in the vertical plane to radiant energy from tungsten filament lamps (8). The samples were ignited with the methane-fueled pilot flame (9).

The atmosphere in the glass cylinder was sampled via the sampling tube (10), which was positioned behind the specimen and at the level of the midsection of the specimen. A vacuum pump continuously pulled chamber atmosphere from the sampling tube at a flow rate of 200 ml/min through one loop of a two loop sampling device. The other loop was connected directly to the injection port of the gas chromatograph. Injection was performed by switching the device such that the roles of the two loops were reversed. In this manner a small constant aliquot of chamber atmosphere could be injected rapidly and reproducibly.

The gas chromatograph was equipped with a column (stainless steel, three ft by 1/8" O.D.) of 5A molecular sieve, 100/120 mesh, and a thermal conductivity detector. The oven was maintained at 40°C. This analytical system detected only oxygen and nitrogen. Since the molar responses of the thermal conductivity detector to oxygen and nitrogen are equal, integration of the peaks expressed the concentrations of oxygen and nitrogen directly. Integration was performed automatically with a Hewlett-Packard Model 3352 B Laboratory Data System. The response time from sampling port to GC injection port was less than three seconds.

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The two lamps (8) each contained six tungsten filament quartz lamps. With the geometric arrangement of lamps and sample it was possible to generate a continuous range of radiant energy from 0 to 8.5 watts/cm^2 at the sample surface. Power to the lamps was regulated with a 10-turn potentiomater. The lamps were calibrated with a radiant calorimeter which was positioned at the middle of the sample plane. A plot of radiant energy versus potentiometer setting was nearly linear. The power output of the lamps was reproducible to ± 5% for individual settings of the potentiometer. Warm-up time for the lamps, from the time of energization to the time of equilibrium radiant energy, was approximately 10 seconds.

Procedure

The pilot flame (9) was lit with a small torch of methanol-soaked glass wool simultaneous with energization of the lamps. The pilot flame was maintained for as long as necessary to obtain sustained burning of the sample in the absence of the pilot flame. This took from three minutes at 0 watts/cm^2 to a few seconds at 5.0 watts/cm^2 of radiant energy. With the sample burning in a sustained manner, the oxygen concentration was decreased incrementally, raising the nitrogen level simultaneously, so that the total flow rate was not varied more than ± 10%. When the flame was extinguished the two-way valve at the sampling loop device was turned to inject a sample of chamber atmosphere into the gas chromatograph.

Oxygen Extinguishment Indices were determined in triplicate at 0, 2.5 and 5.0 watts/cm^2 of radiant energy. In the case of the bismaleimide

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resin, erratic sample behavior required the performance of more than three runs. The three most reliable runs, as determined by operator judgement, were reported.

Results and Discussion

Polymethylmethacrylate (PMMA) was evaluated in order to determine the level of reproducibility of the instrument, PMMA representing a well-behaved standard material. The oxygen extinguishment indices (OEI values) for triplicate runs of PMMA at 0 and 2.5 watts/cm^2 of radiant energy are shown in Table I. The values indicate that a reproducibility of ± 0.2% oxygen is attainable with well-behaved materials. Well-behaved materials are defined simply, as ones which burn steadily and smoothly.

The glass laminates of MY-720 were well-behaved. The OEI values in Table II reflect this characteristic. The values for 0 and 2.5 watts/cm^2 were of the same consistency as those for PMMA. Some modest spread developed in the 5.0 watts/cm^2 experiments. At this high flux the vigorous burning and rapid fuel depletion rate required a faster determination of the OEI, which introduced a greater level of error. Comparing the OEI values of MY-720 laminates and PMMA, it is not surprising that the OEI values of MY-720 are considerably higher than those of PMMA. The epoxy resin would be expected to be inherently less flammable than PMMA on the basis of chemical structure and char formation. PMMA has no aromatic structure and forms no char. In addition, the diluent effect of the glass substrate should be substantial.

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The data for both the laminate materials includes percent total weight loss (% ΔW) from the specimen. Since the amount of resin in each laminate was 30 to 40 percent, and therefore, the total fuel content of each specimen was relatively small, it was necessary to achieve extinguishment before a high weight loss had occurred. A condition for an acceptable burn was that the total percent weight loss was $\leq$ 15 percent. The percent weight losses are shown in Tables II and III for the glass laminate materials. For PMMA weight loss was not a consideration because the specimens contained large amounts of fuel and because the material volatilized completely, forming no char.

The bismaleimide laminate was not a well-behaved material. Burning occurred with sputtering and popping. In some cases the specimen sputtered so violently that the flame was extinguished prematurely, requiring relighting. The inconsistent behavior of this laminate is reflected in the results in Table III, which exhibit considerable spread. The values reported in Table III were the results of runs which burned most smoothly. At least as many runs were discarded because of extremely erratic specimen burning. Despite the greater inaccuracy in the M-751 determination, it is apparent that there is no significant difference in the OEI's of M-751 and MY-720 laminates.

Conclusions

An instrument has been developed for the determination of oxygen extinguishment indices of flat nonmelting materials exposed vertically to radiant energy. The instrument was shown to give oxygen extinguishment indices which were reproducible to $\pm$ 0.2 percent oxygen when well-behaved specimens, such as PMMA, were employed.

The behavior of the two glass laminates of M-751 and MY-720 during flaming oxidation differed considerably. The bismaleimide resin laminate (M-751) sputtered and, in general, burned erratically. The epoxy resin laminate (MY-720) burned evenly. Because of the inconsistent behavior of the M-751 laminate, the determination of oxygen extinguishment indices were less accurate than those of MY-720 laminates. The accuracy of this measurement was sufficient, however, to support the conclusion that the two resins did not exhibit significantly different OEI values at 0, 2.5 and 5.0 watts/cm^2 of radiant energy. It is concluded from these results that the requirements of the two laminates for active involvement in existing fires are approximately equal.

References

1. A. Tewarson, R. F. Pion, *Combustion and Flame*, *26*, 85-103 (1976).

TABLE I

OXYGEN EXTINGUISHMENT INDICES OF PMMA

Radiant Energy (watts/cm^2)

0	2.5
16.3	10.3
16.2	10.4
average OEI = 16.1	average OEI = 10.4

TABLE II

OXYGEN EXTINGUISHMENT INDICES OF MY-720 LAMINATE

0 watts/cm^2		2.5 watts/cm^2		5.0 watts/cm^2	
OEI	%ΔW	OEI	%ΔW	OEI	%ΔW
22.6	6.1	16.9	9.2	12.6	13.6
22.8	5.8	17.1	9.6	11.6	14.4
22.7	6.5	16.6	13.8	11.4	11.0
average OEI = 22.7		average OEI = 16.9		average OEI = 11.9	

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TABLE III

OXYGEN EXTINGUISHMENT INDICES OF M-751 LAMINATE

0 watts/cm^2		2.5 watts/cm^2		5.0 watts/cm^2	
OEI	%ΔW	OEI	%ΔW	OEI	%ΔW
22.6	7.5	16.6	11.1	11.7	10.3
21.4	6.9	15.6	10.3	12.1	9.2
24.4	7.1	17.1	12.1	12.8	8.3

average OEI = 22.8   average OEI = 16.4   average OEI = 12.2
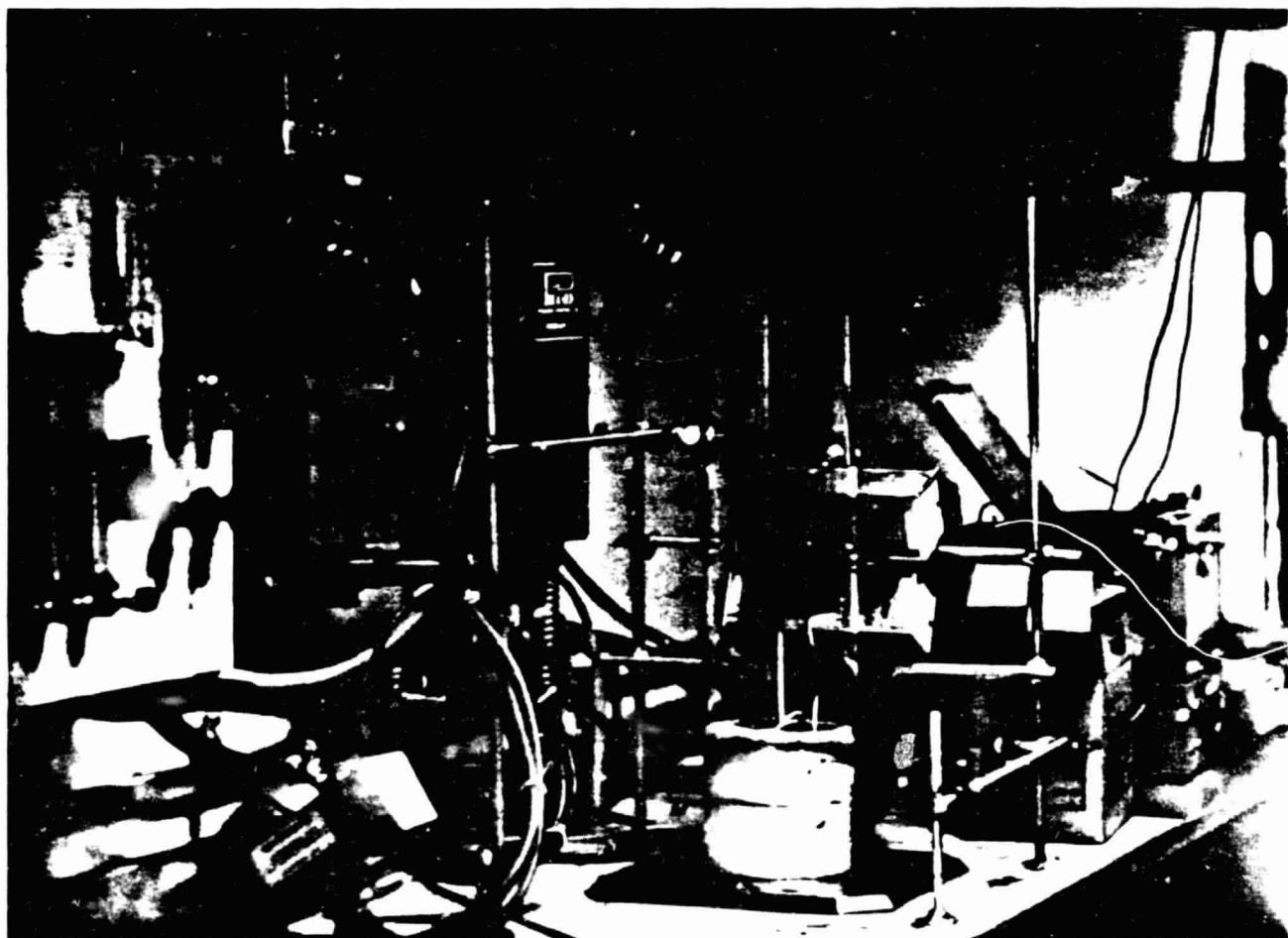
Figure 1. Photograph of instrument for determination of oxygen extinguishment indices as function of radiant energy.

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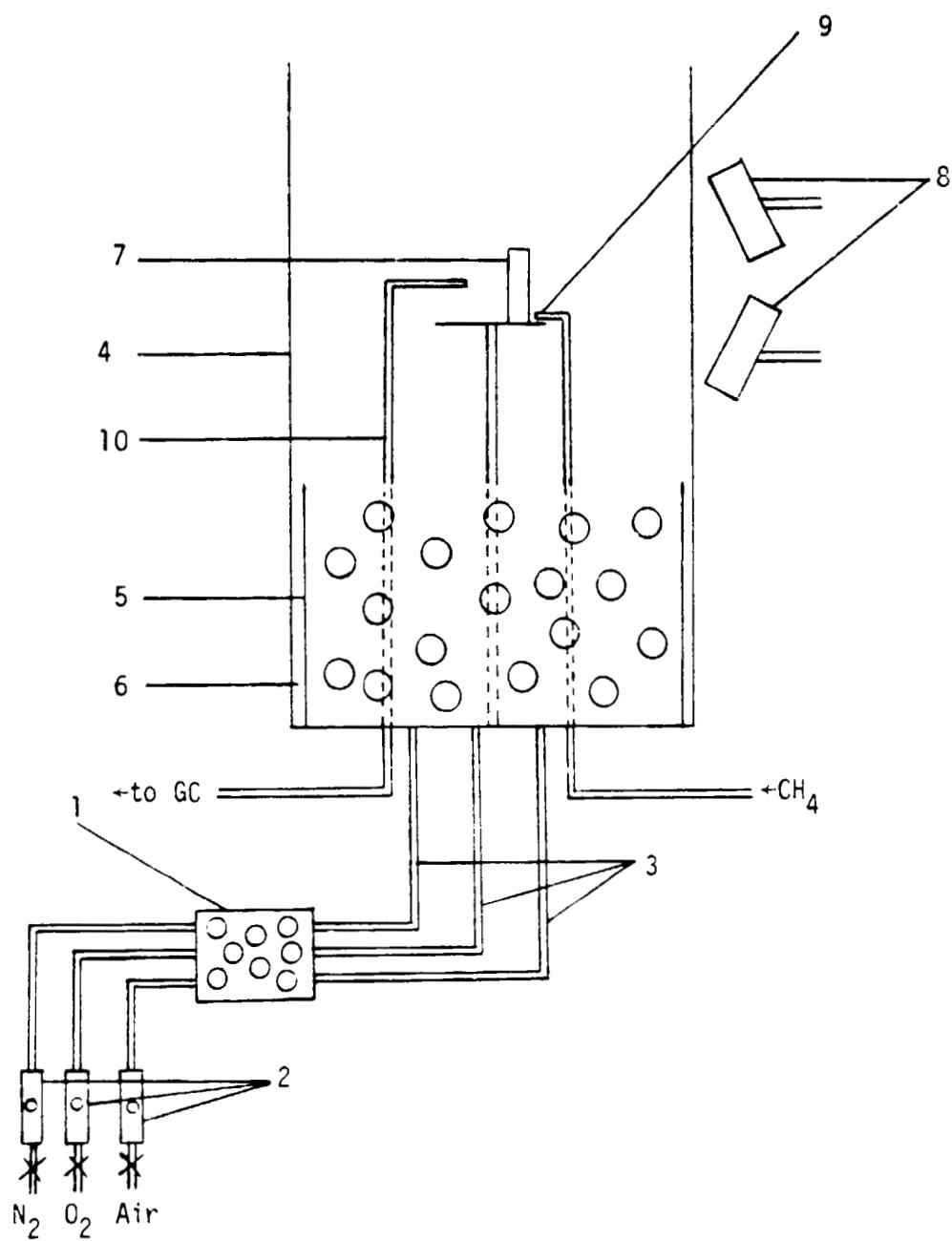
Figure 2.   Schematic of instrument for determination of oxygen

extinguishment indices.

LIST OF COMPONENTS FOR EXPERIMENTAL APPARATUS IN

FIGURE 2.

1. mixing chamber - composed of 1/4 inch thick polymethylmethacrylate 8" X 3" X 3", filled with glass spheres of 1 cm diameter.

2. flow meters, Matheson Gas Products, East Rutherford, N.J. 07073, P.O. Box 85, 932 Paterson Plank Road.

3. three gas inlet lines (tygon tubing) to bottom of glass cylinder, symmetrically spaced.

4. pyrex glass cylinder 17.5 cm O.D., wall thickness 3 mm, 60 cm long.

5. stainless steel cylinder, 16.7 cm O.D., wall thickness, 3 mm, 15.0 cm long.

6. dead space filled with asbestos matting and glass wool.

7. NBS-Aminco Smoke Density sample holder and sample.

8. Model 5208 high density radiant heaters, Research Incorporated, Box 24064, Minneapolis, Minnesota 55424. Lamps powered by a Model 646 Phaser power controller, Research Incorporated.

9. pilot flame (CH_4 gas) apparatus; constructed of a horizontal tube closed at both ends with a single line of holes; produced a flame the length of the bottom of the specimen.

10. atmosphere sampling tube, stainless steel, 1/8" O.D. tubing.

SECTION IV

Comparative Toxicological Evaluation of the Combustion Products

of Glass Laminates of an Epoxy Resin MY-720 and a

Bismaleimide Resin M-751

D. G. Farrar
T. L. Blank

Section IV

Comparative Toxicological Evaluation of the Combustion Products
of Glass Laminates of an Epoxy Resin MY-720 and a
Bismaleimide Resin M-751

Introduction

The Flammability Research Center has developed and standardized a
screening protocol designed to determine the toxicity of the combustion
products of materials [1]. A wide range of materials, differing in both
their physical and chemical properties, have been tested in this proto-
col [1, 2, 3]. The primary objectives of these experiments have been to
determine the absolute toxicity of the combustion products of materials
and to determine, where possible, the cause of the observed toxicity.
Although the effects of toxicants such as carbon monoxide and hydrogen
cyanide often dominate the observed toxicity, the possibility of a role
for other toxicants in the overall effect always remains. Indeed, there
have been frequent reports of significant contributions of acid gases
[2, 4], aldehydes [5, 6] and more exquisite toxicants [7, 8] to the
overall toxicity of the products of combustion of various materials.

The objectives of the current study were to compare the toxicity of
the combustion products of an epoxy resin with that of a bismaleimide
resin, and to establish the primary causes of the toxicity observed.
This information can then be used in conjunction with the relative flam-
mability and smoke-generating properties of the two materials in the
decision-making process leading to the recommendation of materials with

improved properties for end-use application as structural composite materials in aircraft.

Methods

Combustion Device

Combustion products were generated using the furnace described by Potts and Lederer [6]. This is a vertical closed-end tube furnace in which conductive heat is supplied to the sample by nichrome heating elements. The sample is held in a quartz beaker (12.5 cm high; 6 cm diameter). The temperature of the furnace is controlled by a proportional temperature controller, the temperature at the base of the beaker being detected by a chromel-alumel thermocouple.

Nominal combustion product concentrations were calculated using the following equation:

$$\text{Concentration } (gm/m^3) = \frac{\text{Mass of material consumed}}{\text{Vol. of exposure chamber}}$$

The materials were combusted under the two conditions defined by Potts and Lederer [6]. These were:

1. Non-flaming -- the maximum temperature at which a material can be combusted without autoignition occurring.

2. Flaming -- the minimum temperature at which flaming combustion can be initiated and maintained in the presence of an external ignition source (hot nichrome wire with five drops of ethanol added to the sample).

Loadings of material were varied under the two combustion conditions, to allow a range of combustion product concentrations to be generated.

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Exposure System

The furnace was interfaced with the floor of a 60-liter exposure chamber (Figure 1). The chamber, which was constructed of polymethyl methacrylate, was of a regular octagonal configuration. The chamber was approximately 45 cm high, and had a maximum diameter of approximately 45 cm. A port was present of each of four faces of the chamber, to accommodate the introduction of animal restraining tubes. In this way, rats were exposed to the combustion products in a head-only configuration. The head of each rat was approximately 14 cm above the floor of the chamber. A door on a further face of the chamber provided access to the sample beaker. Two sampling ports which were placed at the level of the animals allowed the withdrawal of aliquots of the atmosphere for gas analyses. The environmental temperature was monitored at the level of the animals using a chromel-alumel thermocouple with an external cold junction as a reference. The output was recorded on a strip chart recorder. An aluminum cone coated with polytetrafluoroethylene was place above the mouth of the furnace. The cone served two functions: 1) to shield the animals from radiant heat produced from the furnace, and 2) to aid in the distribution and mixing of the combustion products by creating convection currents. Previous evaluation of the chamber has shown that the mixing of the combustion products is rapid and that insignificant stratification of the volatile components of the atmosphere exists.

Toxicological Evaluation

Male Long-Evans rats were used in this study. Animals were held in-house for two weeks prior to exposure and were weighed on a regular basis. They were caged individually, with food and water available *ad*
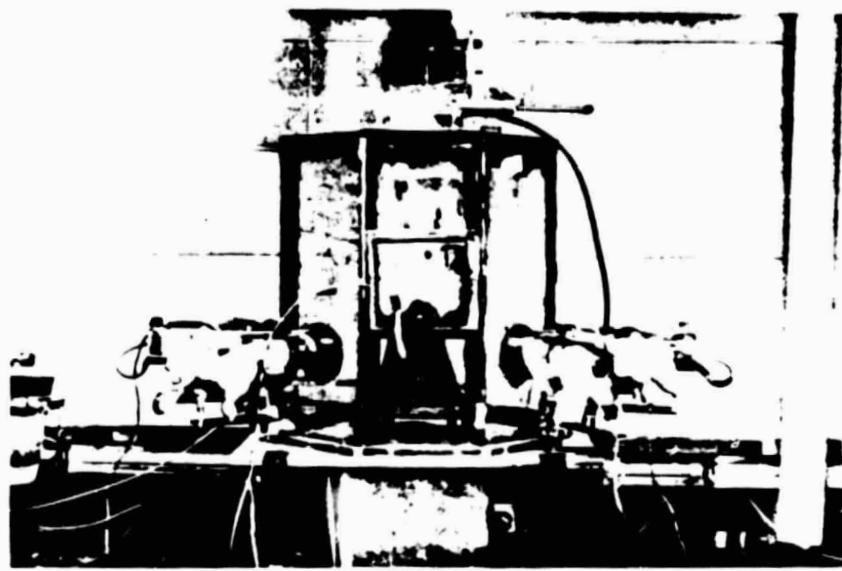
Figure 1. Laboratory-scale furnace/exposure system.

libitum. Rats exhibiting normal growth patterns with a body weight in the range of 400-450 gm were selected for exposure. Individual experiments involved the exposure of four rats to a selected combustion product concentration for a period of 30 minutes. Replicate experiments were conducted at each combustion product concentration. The toxicity was assessed in terms of incapacitation, lethality, the post-exposure recovery of surviving rats and a gross pathological examination of each exposed animal.

Incapacitation. Incapacitation was determined by the assessment of the ability of each rat to perform the leg-flexion avoidance response during exposure to the combustion product atmosphere. This behavioral paradigm requires the training of the rat to avoid the receipt of an electric shock (1-5 milliamps; 10 ms duration; 12.5 hz) which is delivered across the foot. The methodology used for this measurement was similar to that described by Packham *et al* [9]. Rats were trained to perform the response for a period of 15 minutes immediately prior to the exposure. They were then required to perform the response during the entire 30 minute exposure period, or until such time that they were unable to perform the response (continued lack of avoidance for a period of 10 secs), at which time they were considered incapacitated. The time of incapacitation (Ti) for each animal was recorded.

Lethality and Post-Exposure Procedure. The occurrence of any death within the 30 minute exposure was recorded. Surviving animals were retained for a 14 day post-exposure period. Any deaths occurring during this period were also recorded. In addition, surviving rats were observed on a daily basis and their general condition was assessed using

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the criteria detailed in Appendix A. Surviving rats were also weighed on a regular basis throughout the post-exposure period.

Blood Analysis. Two out of each group of four rats that were exposed to the various combustion product atmospheres possessed an indwelling arterial cannula. The cannula was placed into the right femoral artery under barbiturate anesthesia (sodium pentobarbitol) at least 24 hours prior to exposure. Small volumes of arterial blood were drawn from these rats at significant times during the experiment, these being prior to exposure, at Ti, and at the end of the exposure. The blood samples were analyzed for acid/base status (pH), dissolved oxygen content (PO_2) and dissolved carbon dioxide content (PCO_2) using a Radiometer BMS 3MK2 Blood Micro System. The levels of oxyhemoglobin (O_2Hb) and carboxyhemoglobin (COHb) in the blood were also measured using an Instrumentation Laboratories IL-282 CO-Oximeter. In the event of the death of an animal during the exposure, a blood sample was obtained by cardiac puncture at the termination of the experiment for COHb measurement.

Gross Pathology. Each exposed animal was subjected to necropsy. This was conducted either at the time of death (or as soon as possible after death) or, in the case of survivors, 14 days after the exposure. In the latter case, animals were sacrificed with an i. p. injection of sodium pentabarbitol. The evaluation was conducted using a standardized schedule (Figure 2).

Potency of Combustion Atmospheres. A first step comparison between materials was obtained by comparing the overall toxicological potencies of the combustion products in terms of their incapacitating and lethal effects. To obtain this, the relationship between the percentage of the

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Figure 2. Necropsy Report Form.

Autopsy Date _____ _____ By: _____   Exposure Date_____ Animal Weight

Sacrificed ( )   Run _____ Autopsy _____

Dead on Exit ( ) Heart Stick ( ) Animal # _____ Exposure _____

Found Dead ( ) Date _____

EXTERNAL EXAMINATION   Grading scale 1, 2, 3, 4, 5
                                                              —
                                                              5

              Normal

Eyes .   ( )   opaque: L( ) R( ) other _____

Nares: external ( )   blood ( )   fluid ( )   particulates ( )

      internal ( )   blood ( )   fluid ( )   particulates ( )

Mouth: ( )   blood ( )   fluid ( )   particulates ( )

Coat: ( )   diarrhea ( ), blood ( ) where? _____, urine ( )

OTHER ABNORMALITIES ( ) describe on reverse side

INTERNAL EXAMINATION   A edematous   Grading scale 1, 2, 3, 4, 5
                          B hemorrhagic   —
                          C dirty appearance   5
                          D mass(es) present; describe _____

             Normal

Musculature   ( )   pink ( ) other _____

CHEST CAVITY

	Normal	A	B	C	D	Description
Lungs (5 lobes) general external appearance	( )					
Left side left lung	( )					
Right side post. caval lobe	( )					
anterior lobe	( )					
medial lobe	( )					
posterior lobe	( )					
Larynx	( )					
Trachea	( )					
Bronchi (left)	( )					
Bronchi (right)	( )					
Esophagus	( )					

Heart   ( )   blood engorgment ( )

ABDOMINAL CAVITY   Normal   ABNORMALITIES (describe)

  Liver   ( )

  Spleen   ( )

  Left Kidney   ( ) hydronephrotic ( )

  Right Kidney   ( ) hydronephrotic ( )

  Right Testicle   ( ) small ( ) large ( )

  Left Testicle   ( ) small ( ) large ( )

population affected versus the concentration of combustion products was established employing the statistical methodology described by Miller and Tainter [10]. This relationship was obtained for both incapacitation and death. The EC_{50} (concentration causing incapacitation in 50% of the exposed animal population) and LC_{50} (concentration causing death in 50% of the exposed animals) values were calculated for both combustion conditions. The variation of these values was recorded in terms of the standard error (s.e.) of the mean.

Atmosphere Analysis. The concentrations of carbon monoxide (CO), hydrogen cyanide (HCN), carbon dioxide (CO_2) and oxygen (O_2) in the combustion atmospheres were determined by the gas chromatographic analysis of aliquots which were drawn at regular intervals. The details of the analytical procedures used for specific atmospheric constituents are reviewed elsewhere [11]. The levels of CO and HCN detected were expressed in parts per million (ppm). Oxygen and CO_2 levels were expressed as a percentage. The ability of a material to generate a specific toxicant was also assessed in terms of its "toxicant generating capacity" (TGC). This was calculated for specific toxicants using the equation:

$$\text{TGC (mg toxicant/gm material)} = \frac{\text{ppm}^a \times \text{chamber vol.} \times \text{MW} \times 10^{-3}}{\text{sample wt.} \times 25.79^b}$$

a peak level detected.

b mole volume in Salt Lake City,

TGC values for both CO and HCN were derived from each material at the various combustion product concentrations generated and were expressed as the mean value ± standard deviation. These estimates were made for both flaming and nonflaming combustion and corrected for the altitude in

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Salt Lake City. This data was used to calculate the approximate concentrations of CO and HCN at the LC_{50} and EC_{50} values.

Materials

-. The two samples used in this study were supplied by NASA-Ames. Both samples consisted of multi-layers of fiberglass cloth bound together with resin in the form of "prepregs". Each sheet was approximately 3 mm in thickness.

The resin in one sample was an epoxy resin based on methylene dianiline, cured with diamine diphenyl sulphone. This baseline material was identified as MY-720 and is referred to as "the epoxy resin" in the text. The second sample contained a bismaleimide resin based on the reaction of m-maleimido benzoic acid chloride with 4, 4'-diamino diphenyl methane. This sample was identified as M-751 and is referred to as "the bismaleimide resin" in the text.

Results

Combustion Temperature

The furnace temperatures used to achieve combustion of the materials
in the two modes are detailed in Table 1. The nonflaming temperatures
varied substantially between the two materials. The nonflaming temper-
ature the bismaleimide resin was 490°C, whereas that of the epoxy
resin was 600°C. At temperatures above 490°C, the bismaleimide resin
was seen to flash. However, continuous flaming combustion could not be
achieved until the temperature was raised to 700°C. Continuous flaming
combustion was achieved with the epoxy resin at 680°C.

Residue After Combustion

The amount of residue remaining after the combustion of the epoxy
resin was of the order of 75% after both types of combustion. Residues
of 72% and 63% respectively, were obtained with the bismaleimide resin
after nonflaming and flaming combustion. These residue, for the most
part, consisted of the inert fiberglass component of the prepregs. It
was not possible to determine with confidence the presence of char
formation. However the 10 percent difference in the weight of residues
obtained with the bismaleimide resin at the two temperatures suggested
that char formation may have occurred after nonflaming combustion with
this material.

Table 1. The Comparative Toxicant Generating Capacities and Toxicological Potencies in the Rat of the Combustion Product Atmospheres Derived from an Epoxy Resin and a Bismaleimide Resin After Both Nonflaming and Flaming Combustion.

Material	Combustion Condition	Furnace Temperature	Toxicant Generating Capacity		EC_{50} S.E. gms/m^3	LC_{50} S.E. gms/m^3
			mg CO/gm	mg HCN/gm		
EPOXY	NF	600°C	74.6 ± 10.7 n=8	3.2 ± 0.7 n=10	4.1 ± 0.9	11.0 ± 2.1
	F	680°C	50.5 ± 13.1 n=8	2.5 ± 0.6 n=8	6.2 ± 1.0	7.3*
BISMALEIMIDE	NF	490°C	27.5 ± 5.2 n=9	1.4 ± 0.3 n=9	20.1 ± 3.9	41.9 ± 3.2
	F	700°C	35.6 ± 8.7 n=10	2.9 ± 0.9 n=10	6.8 ± 1.5	15.0 ± 2.2

* Insufficient data for S.E. calculation.

Analysis of Combustion Product Atmospheres

Both CO and HCN were detected in the combustion product atmospheres generated from both materials under the two combustion modes. The levels detected, and the time curves of the generation of the two toxicants are illustrated in Figures 3-7. Each point plotted represents the mean levels detected at the various times in at least two experiments.

Epoxy Resin - Nonflaming. Various weights of the epoxy resin were combusted, generating a range of combustion products concentrations varying from 1.4 to 22 gm/m^3. The peak CO levels detected in these atmospheres ranged from 900 ppm to 5000 ppm (Figure 3). HCN was also detected in these atmospheres, the peak levels ranging from 20 ppm to 200 ppm (Figure 4). The peak levels of these two toxicants increased with increasing sample weight. For the most part, the levels of these two toxicants rose rapidly during the first 10 minutes of the exposure, after which they remained approximately stable. The levels of HCN generated from the largest sample of the epoxy resin (22 gm/m^3) peaked after a period of 15 minutes.

The levels of O_2 in the chamber were observed to fall steadily throughout each exposure. The maximum fall was observed at 22 gm/m^3, the O_2 level falling to 19.6 percent. The levels of CO_2 were observed to rise steadily throughout the exposures. Again the maximum change was observed at 22 gm/m^3, the CO_2 level rising to 1.6 percent. The deviations in both O_2 and CO_2 levels were due primarily to the respiratory activity of the exposed rats.

Epoxy Resin - Flaming. Various weights of the epoxy resin were combusted, generating combustion product concentrations ranging from

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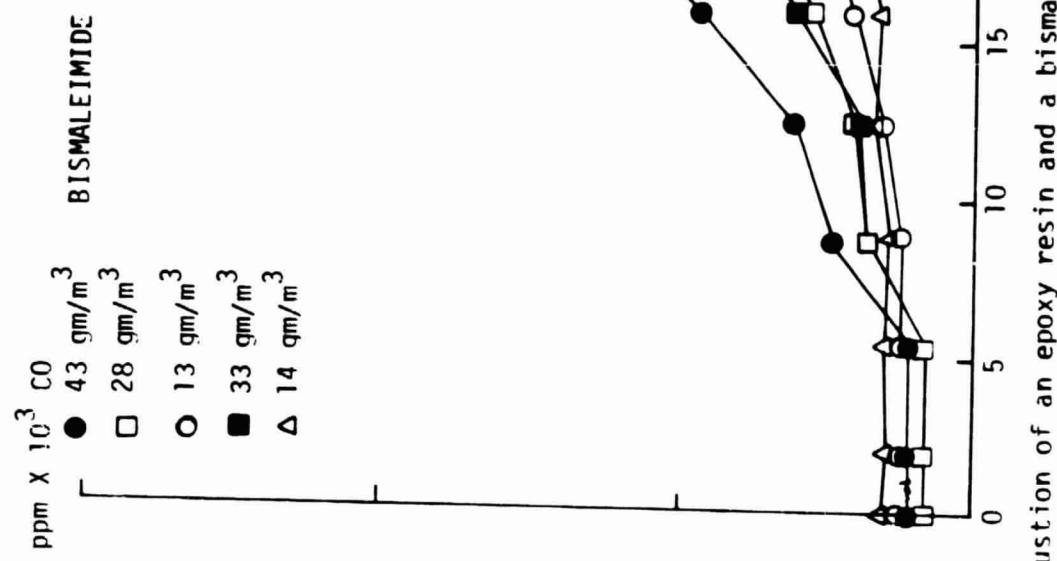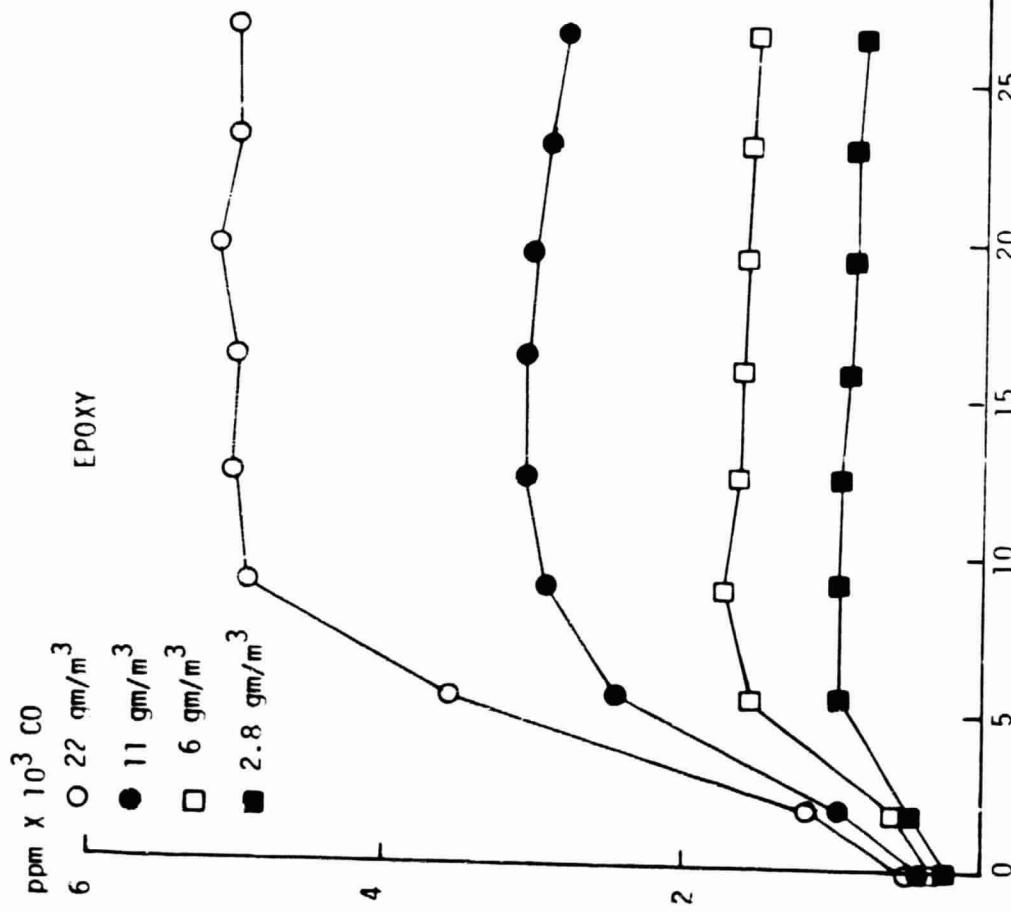
Figure 5. Carbon monoxide generation from the nonflaming combustion of an epoxy resin and a bismaleimide resin.
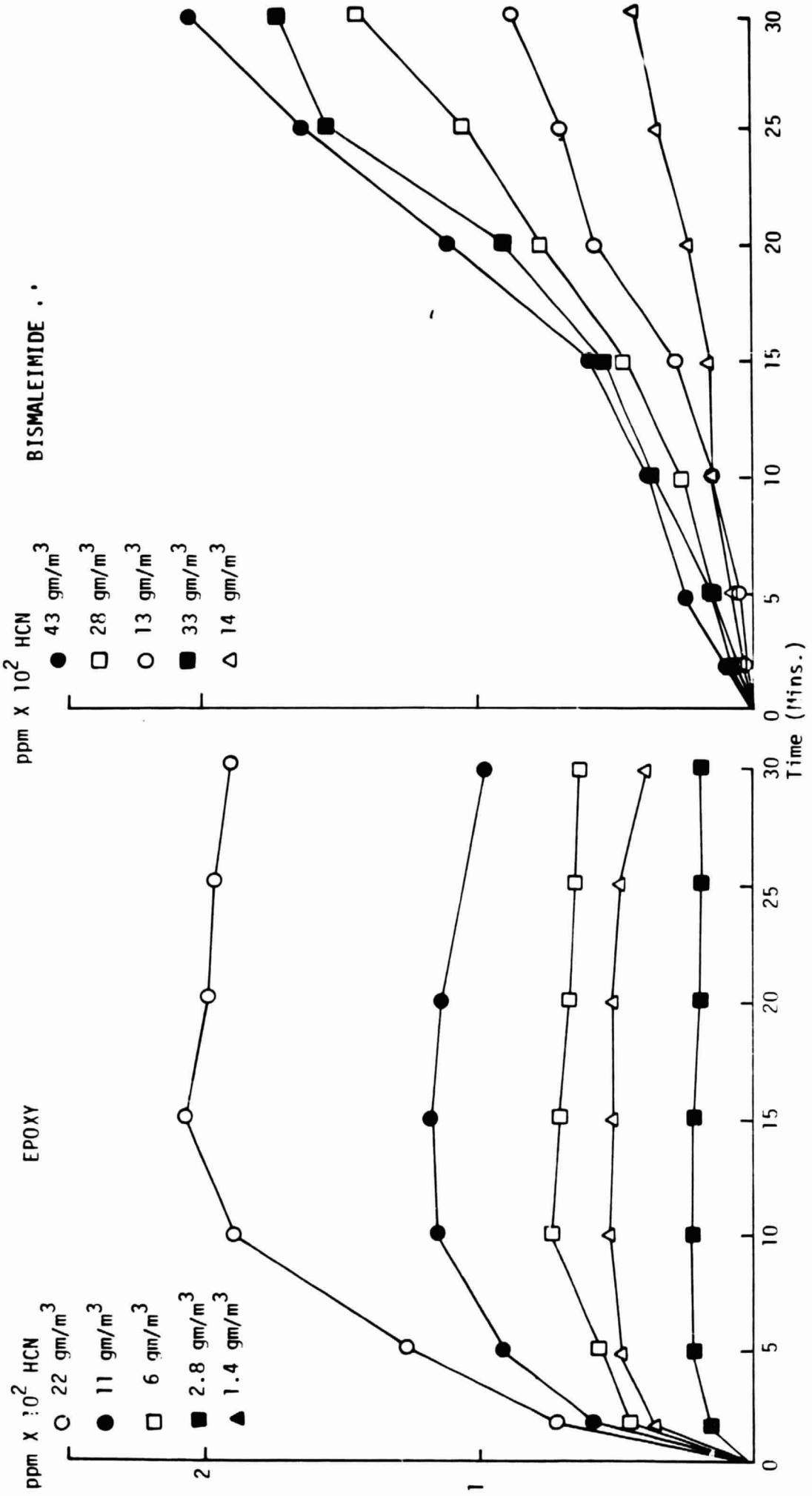
Figure 4. Hydrogen cyanide generation from the nonflaming combustion of an epoxy resin and a bismaleimide resin.

3.1 to 21.9 gm/m^3. The peak levels of carbon monoxide (Figure 5) and hydrogen cyanide (Figure 6) detected in these atmospheres ranged from 750 ppm to 3200 ppm and from 25 ppm to 165 ppm respectively. The peak levels of these two toxicants increased with increasing sample weight. Peak levels were detected after 10 minutes, after which the levels remained reasonably stable.

The fall in O_2 levels in these experiments was somewhat greater than in a control experiment (no combustion). The maximum fall was observed at 21.9 gm/m^3, where the O_2 level fell to 17.4 percent. Small steady increases in CO_2 levels were also detected, after an initial sharp rise, these again being greater than that observed in the control experiment. The maximum increase was observed at 11.1 gm/m^3, where the CO_2 levels increased to 4.1 percent. The fact that these changes were considerably greater than those in the control experiment suggested that O_2 consumption and CO_2 generation occurred during the combustion.

Bismaleimide Resin - Nonflaming. Varying weights of the bismaleimide resin were combusted, generating combustion product concentrations ranging from 13 to 43 gm/m^3. These combustion product atmospheres contained peak levels of CO ranging from 1100 ppm to 4200 ppm (Figure 3). Hydrogen cyanide was also detected in these atmospheres, the peak levels ranging from 40 ppm to about 200 ppm (Figure 4).

The peak levels of these two toxicants for the most part, increased with increasing sample weight. However, the time course of the generation of both toxicants was considerably slower than for the epoxy resin. At all combustion product concentrations studied, the CO levels did not rise above the minimal detectable limits for a period of at

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Figure 5. Carbon monoxide generation from the flaming combustion of an epoxy resin and a bismaleimide resin.
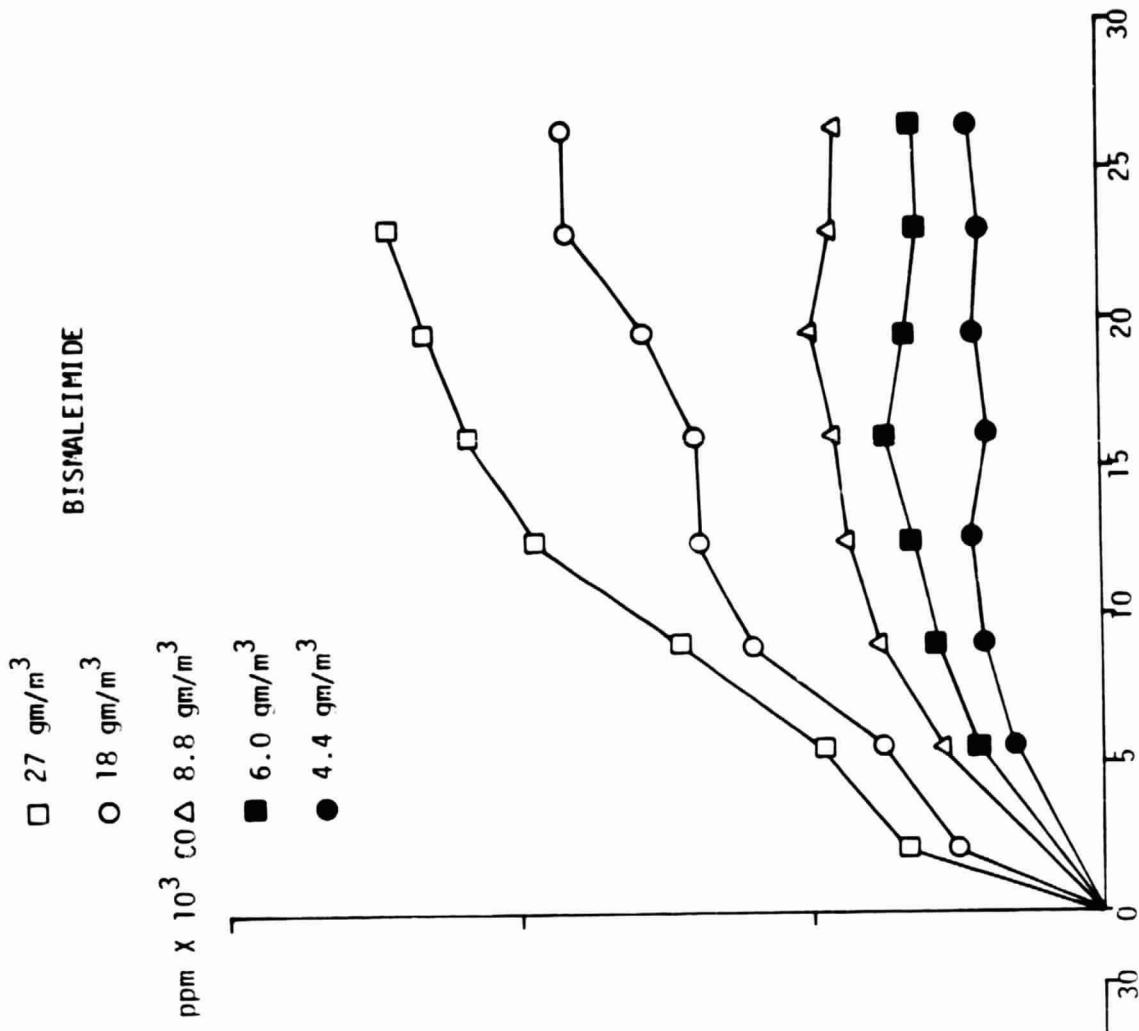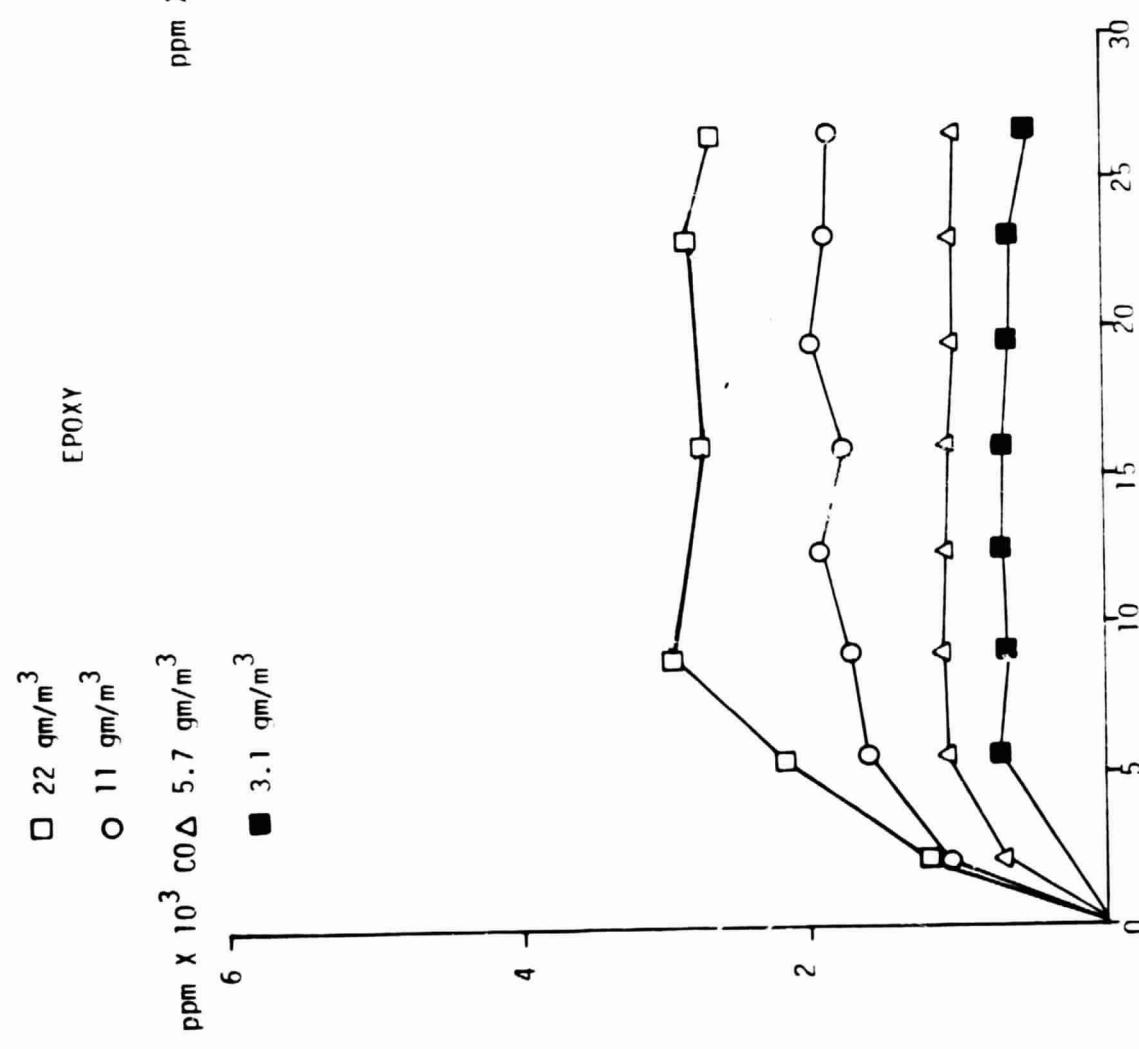
Figure 6. Hydrogen cyanide generation from the flaming combustion of an epoxy resin and a bismaleimide resin.
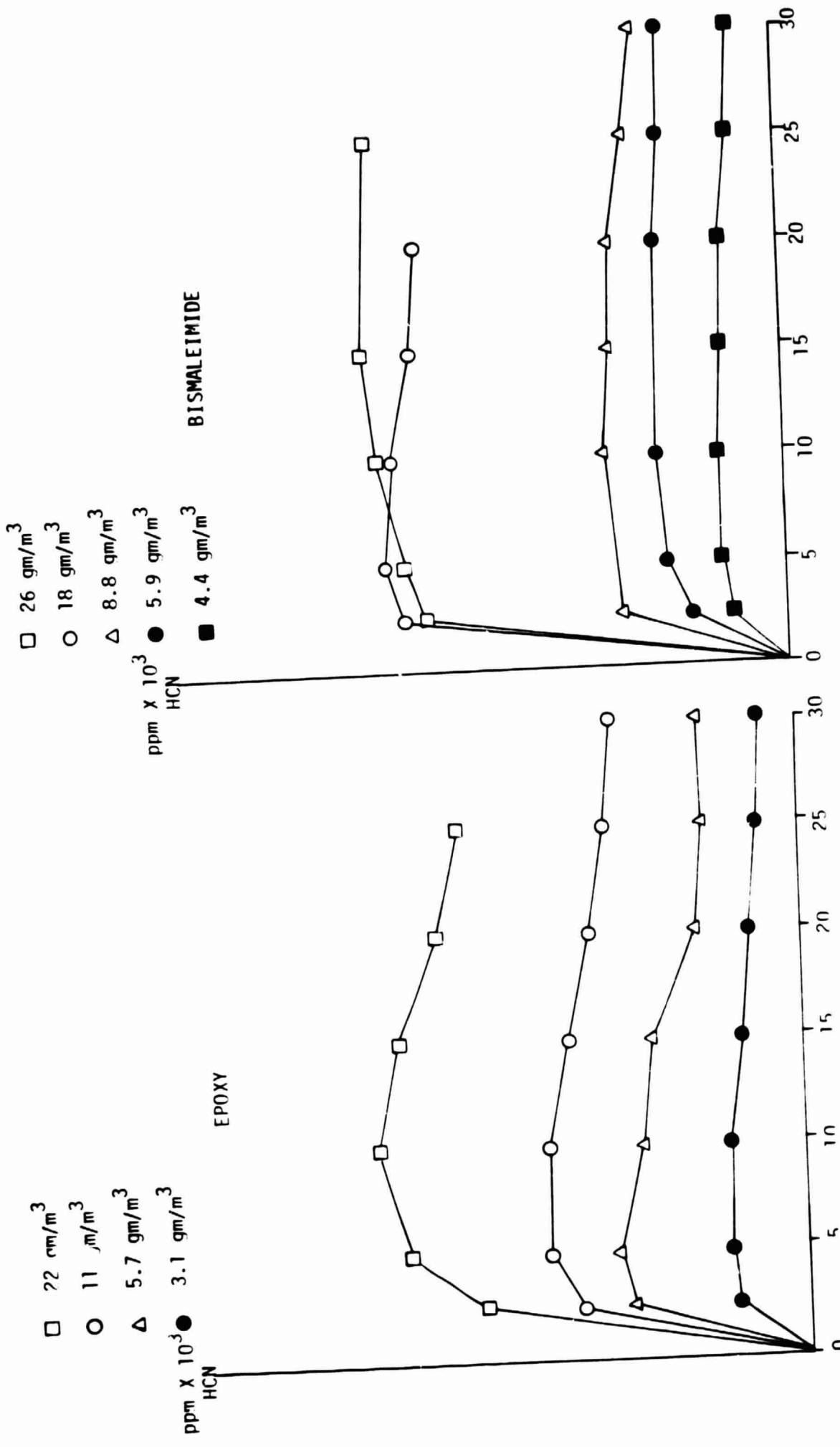
least 5.5 minutes. A slow generation of CO was subsequently detected over the following seven minutes, after which the levels began to rise at a faster rate. Peak levels were always detected at the end of the exposure (30 minutes). The levels of HCN were also observed to rise slowly for the first 15 minutes of each exposure, after which they began to rise more rapidly. The peak levels, which also increased with increasing sample weight, were always detected at the end of each exposure.

As with the epoxy resin in this combustion mode, the observed decreases in O_2 levels and increases in CO_2 levels were not large. The maximum changes were observed at 43.1 gm/m^3, in which the O_2 level fell to 19.8 percent, and the CO_2 level increased to 1.6 percent.

Bismaleimide Resin - Flaming. Varying weights of the bismaleimide resin were combusted, producing combustion product concentrations ranging from 4.4 to 26.5 gm/m^3. The peak levels of CO (Figure 3) and HCN (Figure 6) detected in these combustion product atmospheres ranged from 900 ppm to 4900 ppm and from 25 ppm to 160 ppm, respectively. For the most part, the peak levels of these two toxicants increased with increasing sample weight. The one exception to this, however, was with the two highest concentrations studied (17.6 and 26.5 gm/m^3) which contained similar levels of HCN (160 ppm).

The time course of the generation of CO was more rapid than after nonflaming combustion, but was still slower than that observed with the epoxy resin in this combustion mode. At the lowest combustion product concentration (4.4 gm/m^3), the peak CO level was detected at 12.5 minutes into the exposure. As the sample weight was increased, the peak CO

level was detected progressively later into the exposure. At the highest combustion product concentration (26.5 gm/m^3) the peak CO level was ..ot detected until 23.5 minutes into the exposure. In contrast to this, HCN was generated very rapidly in these experiments. In most exposures, the HCN levels peaked after 5 - 10 minutes. The noteable exception to this was at the highest combustion product concentration (26.5 gm/m^3), were the peak HCN level was not detected until 15 minutes into the exposure. However, at both this concentration and at 17.6 gm/m^3, the majority of the total HCN to be generated was formed during the first two minutes of the exposure.

The levels of O_2 and CO_2 in these experiments were observed to deviate slightly from a control experiment, suggesting that O_2 was consumed and the CO_2 was generated by the combustion. The maximum changes were seen at 26.5 gm/m^3, in which the O_2 levels fell to 18.5 percent and the CO_2 level increased to 3.1 percent.

Toxicant Generating Capacity (TGC). The TGC values in terms of CO and HCN for the two materials under the two combustion conditions are shown in Table I. Because the levels of CO and HCN did not stabilize after the nonflaming combustion of the bismaleimide resin, the TGC values calculated for this combustion mode are not a true representation of the full capacity of the material to generate these two toxicants under this combustion condition. However, they do represent the performance of the material within a limited time-frame, and therefore have value for comparative purposes within the confines of this experiment.

The TGC values illustrated that the epoxy resin produced somewhat more of both CO and HCN per gram of material after nonflaming combustion,

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than after flaming combustion. The bismaleimide resin produced approximately 2.5 times less CO and HCN per gram of material than the epoxy resin after nonflaming combustion (within the time-course of the experiment), but produced considerably more CO and HCN per gram of material than the epoxy resin after flaming combustion.

Toxicity of the Combustion Product Atmospheres

The EC_{50} and LC_{50} values for the two materials under the two combustion conditions are compared in Table 1. The various responses of individual groups of rats exposed to the various concentrations of combustion products of the two materials are detailed in Tables 2 and 3, along with a summary of the atmospheric levels of the various measured toxicants at each exposure level. The toxicant levels (CO and HCN) reported for the epoxy resin are the mean of the measured values over the last 20 minutes of the exposure. Those for the bismaleimide resin are the peak values measured (usually at the end of each exposure). The levels of O_2 and CO_2 reported in Tables 2 and 3 are the mean of the levels measured during the last 20 minutes of the exposure.

Incapacitation. Concentration-related incapacitation (loss of the leg-flexion avoidance response) was observed on exposure to combustion product atmospheres from both materials under both combustion conditions. The effective concentration range for the epoxy resin was 1.4 - 11.1 gm/m^3 after nonflaming combustion, and 3.1 to 11.1 gm/m^3 after flaming combustion. Incapacitation was only observed after exposure to higher combustion product concentrations of the bismaleimide resin, however. The effective ranges for this material were 13.2 - 43.1 gm/m^3 after nonflaming combustion and 4.4 - 17.6 gm/m^3 after flaming combustion.

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Table 2. Summory of the Atmospheric Analyses, the Resulting Incapacitation and the Blood Chemistry Status at Ti in Rats Exposed to the Nonflaming and Flaming Combustion Products of an Epoxy Resin.

Concentration (gm/m^3)	Nonflaming						Flaming				
	Control	1.4	2.8	5.5	11.1	22.0	Control	3.1	5.7	11.1	21.9
Atmospheric Analysis											
O_2 (%) (mean)	20.1	20.5	20.5	20.1	20.1	19.6	20.5	20.2	19.8	18.9	17.4
CO_2 (%) (mean)	0.9	1.1	1.1	1.4	1.3	1.6	1.0	1.4	1.6	4.1	3.5
CO ppm (mean)	430	540	880	1600	2950	5050	280	650	1090	1890	2740
HCN ppm (mean)	-	19	45	62	101	196	-	22	49	85	149
Incapacitation											
# Animals Exposed	4	8	8	8	8	8	4	8	8	8	8
# Animals Incapacitated	0	0	2	5	8	8	0	0	2	8	8
Mean Ti - Seconds (S.D.)	-	-	1283	1355	975	684	-	-	1188	839	698
(S.D.)				(562)	(100)	(462)	(143)			(81)	(258)	(141)
Blood Chemistry at Ti											
n=	0	0	0	2	4	4	0	0	0	4	4
O_2Hb (mean)		-	-	43.2	46.4	33.4	-	-	-	42.9	37.6
COHb (mean)	-	-	-	49.5	44.4	60.9	-	-	-	52.1	53.7
pH (mean)	-	-	-	7.31	7.18	7.05	-	-	-	7.34	7.09
PCO_2 (mean)	-	-	-	29.0	28.5	30.3	-	-	-	24.0	34.9
PO_2 (mean)	-	-	-	85.2	91.6	81.4	-	-	-	71.0	65.8

Table 3. Summary of the Atmospheric Analyses, the Resulting Incapacitation and Blood Chemistry Status at Ti in Rats Exposed to the Nonflaming and Flaming Combustion Products of a Bismaleimide Resin.

Concentration (gm/m^3)	Nonflaming						Flaming					
	Control	13.2	14.4	28.3	33.0	43.1	Control	4.4	6.0	8.8	17.6	26.5
Atmospheric Analysis												
O_2 (%) (mean)	20.3	20.3	20.7	20.2	20.4	19.8	20.0	20.1	19.9	19.3	19.2	18.5
CO_2 (%) (mean)	0.9	1.4	1.0	1.4	1.3	1.6	1.3	1.3	1.8	2.0	2.3	3.1
CO ppm (peak)	<480	1635	733	2295	2765	4195	<360	940	1405	2005	3700	4905
HCN ppm (peak)	-	87	44	144	178	206	-	26	51	66	162	162
Incapacitation												
# Animals Exposed	4	8	8	8	7	12	4	8	8	8	8	8
# Animals Incapacitated	0	0	3	7	7	11	0	0	5	7	8	8
Mean Ti - Seconds	0	0	1102	1227	1257	1244	0	0	1398	935	941	746
(S.D.)			(549)	(172)	(531)	(325)			(184)	(477)	(387)	(198)
Blood Chemistry at Ti												
n=	0	0	1	4	1	5	0	0	2	4	4	3
O_2Hb (mean)	-	-	76.6	58.5	49.2	40.2	-	-	50.7	52.7	36.2	32.7
COHb (mean)	-	-	2.7	24.7	43.6	58.3	-	-	44.2	34.6	48.4	59.3
pH (mean)	-	-	7.23	7.36	7.20	7.10	-	-	7.34	7.33	7.12	7.05
PCO_2 (mean)	-	-	35.3	34.3	23.9	34.2	-	-	27.4	28.3	24.8	37.2
PO_2 (mean)	-	-	74.5	76.3	76.8	80.4	-	-	76.7	81.7	80.2	64.8

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Comparison of the EC_{50} values for the two materials (Table I) showed that they were equipotent in terms of their incapacitation potential after flaming combustion, but that the epoxy resin was five times more potent in this respect than the bismaleimide resin after nonflaming combustion. The incapacitating potency of the epoxy resin did not change signficantly between combustion conditions. The bismaleimide resin, however was three times more potent after flaming than after nonflaming combustion.

Time to Incapacitation (Ti). The Ti values for all rats incapacitated on exposure to the combustion products of the two materials are detailed in Figures 7 and 8. Large variations in the Ti values were seen in these experiments. The majority of the rats incapacitated on exposure to the nonflaming combustion products of the epoxy resin had Ti values greater than 10 minutes (Figure 7). Two rats were incapacitated in a shorter time period, however, these two animals being in the groups exposed to the two highest combustion product concentrations employed. A slightly higher proportion (5/18) of the rats incapacitated by the flaming combustion products of this material had Ti values of less than 10 minutes.

Rats exposed to the nonflaming combustion products of the bismaleimide resin tended to become incapacitated later in the exposure. The majority of the rats (20/29) had Ti values greater than 20 minutes. The distribution of Ti values in rats exposed to the flaming combustion products of this material was more like that seen with the epoxy material, with the majority (23/28) having Ti values greater than 10 minutes. As with the epoxy resin, a low incidence of rats incapacitated within the

89

% COHb at Ti

FLAMING

21.9 gm/m^3 ●
11.1 gm/m^3 +
5.7 gm/m^3 ○

100

80

60

40

20

Ti - Secs

500   1000   1500   1800

% COHb at Ti

NONFLAMING

22.0 gm/m^3 ●
11.1 gm/m^3 +
5.5 gm/m^3 ○
2.8 gm/m^3 ×

100

80

60

40

20

Ti - Secs

500   1000   1500   1800
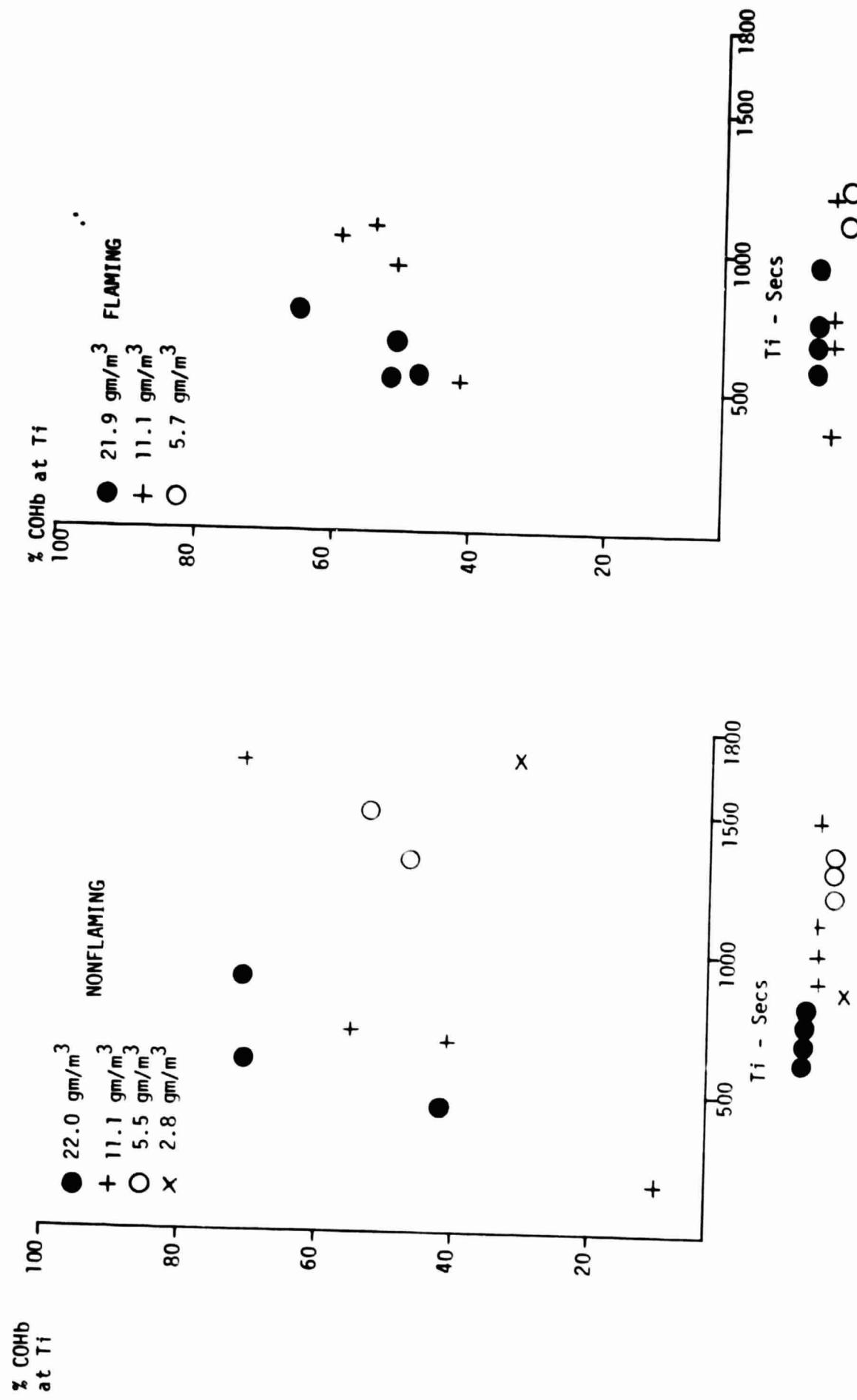
Figure 7. The relationship between time to incapacitation (Ti) and carboxyhemoglobin levels (% COHb) at Ti for rats incapacitated on exposure to various concentrations of a) the nonflaming and b) the flaming combustion products of an epoxy resin (data points presented below the x-axis represent Ti values in non-cannulated rats).
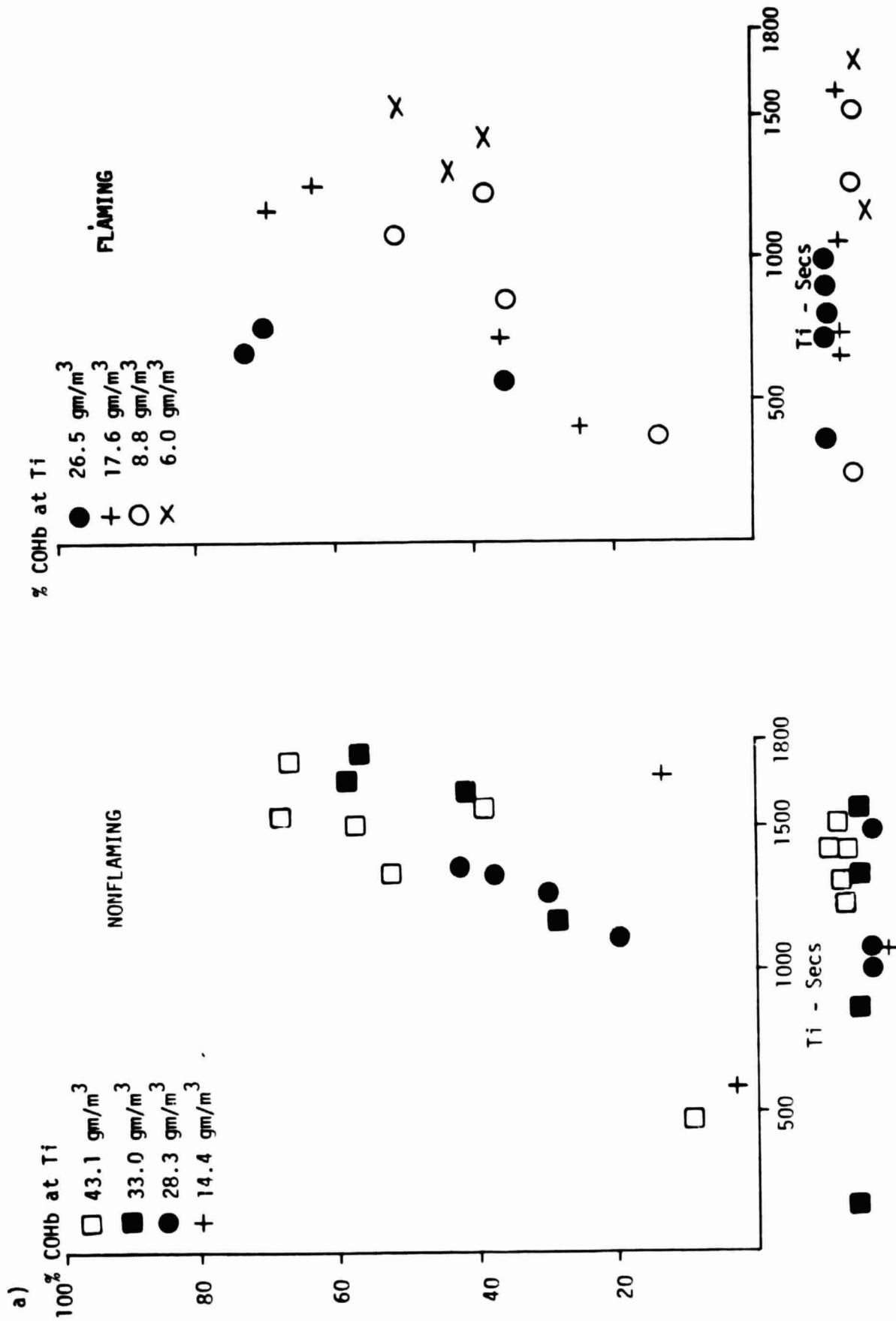
Figure 8. The relationship between time to incapacitation (Ti) and carboxyhemoglobin levels (% COHb) at Ti for rats incapacitated on exposure to various concentrations of a) the nonflaming and b) the flaming combustion products of a bismaleimide resin (data points presented below the x-axis represent Ti values in non-cannulated rats).

first 10 minutes of the exposure was seen in both combustion conditions (3/29 - nonflaming; 5/28 - flaming).

The mean Ti values for the groups of rats incapacitated upon exposure to the various combustion product concentrations of the two materials are shown in Tables 2 and 3. Valid comparison between these Ti values can be made at concentrations of equal toxicological impact. For this purpose, concentrations causing incapacitation in at least seven out of the eight animals exposed were compared. Comparing the lowest concentration for each material that caused this degree of involvement (Tables 2 and 3) showed that the mean Ti values for these specific groups were somewhat shorter for the epoxy resin than for the bismaleimide resin. However, because of the wide variation in Ti for rats exposed to the same environment, the differences in the mean Ti values were not large enough to appear significant. It was interesting to note that exposure of rats to twice the maximally incapacitating concentration of nonflaming epoxy resin combustion products (22.0 gm/m^3) caused a marked reduction in Ti for this group of rats. This trend was not evident after the flaming combustion of this material, nor with either combustion mode of the bismaleimide resin.

Blood Chemistry at Ti. A summary of the blood chemistry status at Ti in rats exposed to the combustion products of the two materials is presented in Tables 2 and 3. The relationships between Ti and percent COHb at Ti for the cannulated rats are shown in Figures 7 and 8. The majority of rats incapacitated on exposure to the nonflaming combustion products of the epoxy resin had COHb values in excess of 40 percent (Figure 7a). There were two exceptions to this. One rat that was

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incapacitated very early (180 secs) on exposure to 11.1 gm/m^3 had a COHb level of 10 percent at Ti. A further rat, that was exposed to 2.8 gm/m^3 was incapacitated towards the end of the exposure (1700 secs) with a COHb level of 31 percent. All of the rats that were incapacitated on exposure to the flaming combustion products of the epoxy resin had COHb levels in excess of 40 percent at Ti.

A greater proportion of the rats exposed to the combustion products of the bismaleimide resin had very low COHb levels at Ti. Eight of the total of 16 cannulated rats exposed to the nonflaming combustion products had COHb levels less than 40 percent at Ti. The Ti values for these rats varied from 460 secs to 1680 secs. Two of these rats, which were incapacitated in less than 10 min, had COHb levels of less than 10 percent. The remaining rats, whose COHb levels were in excess of 10 percent, were incapacitated during the last eight minutes of the exposures. A similar profile was seen in rats incapacitated on exposure to the flaming combustion products of the bismaleimide resin. One rat, out of a total of 14, was incapacitated early in the exposure with a low COHb level. A further six rats had COHb levels that ranged between 10 - 40 percent. The remaining seven rats had COHb levels in excess of 40 percent at Ti.

The remaining changes in blood chemistry status were more consistant between the materials. Falls in O_2Hb levels were observed. For the most part these falls reflected the various degrees of loading of CO onto the hemoglobin in individual rats. The PO_2 and PCO_2 levels did not change significantly from control values at Ti. Significant falls in blood pH were observed at Ti, however. This effect was seen with both

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materials under both combustion conditions. As the combustion product
concentration increased, with each material, the degree of depression of
blood pH at Ti was also seen to increase.

Blood Chemistry at the End of the Exposure. The state of the blood
chemistry in surviving cannulated rats at the end of the 30 minute
exposure is summarized in Tables 4 and 5. Exposure of rats to the two
materials under both combustion conditions resulted in similar blood
chemistry profiles at the end of the exposure. The levels of COHb were
increased, the degree of increase being directly related to the com-
bustion product concentration. The changes in COHb levels were accom-
panied by appropriate falls in O_2Hb levels at all combustion product
concentrations (i.e., COHb + O_2Hb → 100%). The PO_2 and PCO_2 levels
usually remained normal, with slight increases in PO_2 levels at the
highest combustion product concentrations generated from each material
under the two combustion conditions. Significant falls in pH were also
observed at the higher combustion product concentrations. Again, the
degree of fall in pH was seen to increase with the combustion product
concentration. Rats exposed to the higher concentrations of the non-
flaming combustion products of the two materials showed a greater fall
in pH than those exposed to the flaming combustion products.

Lethality. Concentration-related death was also obtained in these
experiments. Deaths during the exposure were observed in rats exposed
to nonflaming combustion product concentrations of the epoxy resin that
were greater than 5.5 gm/m^3. No post-exposure deaths were recorded in
rats exposed to these combustion products. After flaming combustion of

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Table 4. Summary of the Deaths Resulting from the Exposure of Rats to the Nonflaming and Flaming Combustion Products of an Epoxy Resin, and the Blood Chemistry Status in Surviving Rats Observed at the End of the Exposure.

Concentration (gm/m^3)	Nonflaming						Flaming				
	Control	1.4	2.8	5.5	11.1	22.0	Control	3.1	5.7	11.1	21.9
Death											
# Exposure Deaths	Ö	0	0	0	4	8	0	0	1	4	8
% COHb at death - mean	-	-	-	-	72.9	78.1	-	-	-	64.7	64.2
(S.D.)					(3.6)	(3.5)				(0.6)	(12.6)
# Post-Exposure Deaths	0	0	0	0	0	0	0	1	0	3	0
Total # Deaths	0/4	0/8	0/8	0/8	4/8	8/8	0/4	1/8	1/8	7/8	8/8
Blood Chemistry at End of Exposure (30 minutes)											
n=	2	4	4	4	4	0	2	4	4	2	0
O_2Hb (mean)	87.8	75.7	63.3	39.8	27.1	-	86.5	67.5	32.2	31.6	-
COHb (mean)	2.3	16.9	30.5	49.4	69.2	-	1.7	27.8	53.1	63.3	-
pH (mean)	7.47	7.44	7.33	7.10	6.86	-	7.44	7.44	7.38	7.14	-
PCO_2 (mean)	22.0	22.3	25.4	24.8	23.9	-	23.0	26.6	23.6	22.4	-
PO_2 (mean)	64.8	83.0	77.9	72.9	92.5	-	72.1	71.7	73.6	83.7	-

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Table 5. Summary of the Deaths Resulting from the Exposure of Rats to the Nonflaming and Flaming Combustion Products of a Bismaleimide Resin and the Blood Chemistry Status in Surviving Rats Observed at the End of Exposure.

Concentration (gm/m^3)	Control	13.2	14.4	28.3	33.0	43.1	Control	4.4	6.0	8.8	17.6	26.5
Death												
# Exposure Deaths	0	0	0	0	2	6	0	0	0	0	6	8
% COHb at Death - mean	-	-	-	-	63.7	70.3	-	-	-	-	69.0	76.0
(S.D.)					(4.5)	(1.9)					(8.3)	(2.3)
# Post-Exposure Deaths	0	0	0	0	0	0	0	0	0	0	0	0
Total # Deaths	0/8	0/8	0/8	0/8	2/7	6/12	0/8	0/8	0/8	0/8	6/8	8/8
Blood Chemistry at End of Exposure (30 minutes)												
(n=)	2	4	4	4	4	6	2	3	4	4	0	0
O_2Hb (mean)	84.6	48.2	74.2	38.0	47.6	27.9	87.3	59.5	46.9	35.5	-	-
COHb (mean)	1.3	47.3	14.2	56.3	46.2	65.6	1.5	34.0	50.4	60.4	-	-
pH (mean)	7.36	7.40	7.32	7.19	7.06	6.84	7.43	7.41	7.36	7.23	-	-
PCO_2 (mean)	36.1	20.6	29.2	25.3	26.1	29.1	22.3	27.3	25.7	18.1	-	-
PO_2 (mean)	74.3	73.8	81.2	78.7	80.1	86.3	88.0	83.1	80.1	94.8	-	-

the epoxy resin, however, deaths were recorded at all concentrations employed (Table 4). Deaths during the exposure were recorded at 5.7 gm/m^3 and above. Post-exposure deaths were also recorded. One rat died one day after exposure to 3.1 gm/m^3, and three post-exposure deaths were recorded in rats exposed to 11.1 gm/m^3. These deaths were recorded on days 2, 3 and 4 post-exposure.

The exposure of rats to the combustion products of the bismaleimide resin, both flaming and nonflaming, resulted in deaths occurring during the exposure. No post-exposure deaths were recorded. Nonflaming combustion products caused death at concentrations of 33 gm/m^3 and above (Table 5). Exposure of rats to the flaming combustion products of the bismaleimide resin resulted in death at concentrations of 17.6 gm/m^3 and above.

Comparison of the LC_{50} values of the two materials (Table 1) showed that the combustion products of the epoxy resin were more lethal than those of the bismaleimide resin. After nonflaming combustion, the epoxy resin was four times more toxic than the bismaleimide resin. This potency difference was reduced to a two-fold difference after flaming combustion.

COHb Levels At Death. The percent COHb levels of rats dying during the exposure are detailed in Tables 4 and 5. The mean levels in groups of rats dying on exposure to the various lethal concentrations of the two materials ranged from 63.7 percent to 78.1 percent.

Post-exposure Observations. The general state of surviving rats was assessed immediately after the exposure in each experiment. The observations are summarized in Tables 6 and 7.

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Table 6. Summary of the Observations on the General State of Rats Immediately Following Exposure to the Nonflaming and Flaming Combustion Products of an Epoxy Resin.

	Number of animals showing abnormal responses								
	Nonflaming					Flaming			
Concentration (gm/m^3)	1.4	2.3	5.5	11.1	22.0	3.1	5.7	11.1	21.9
Observations (group size = 8)									
# Incapacitated	0	2	5	8	8	0	2	8	8
# Deaths During Exposure	0	0	0	4	8	0	1	4	8
Behavior									
↓ Activity	0	0	4	4	-	4	5	4	-
↑ Sensitivity to Touch	0	0	0	1	-	0	1	0	-
↓ Pain (Tail Pinch)	0	1	1	0	-	1	0	0	-
↓ Nuzzle Response	0	0	1	0	-	0	0	1	-
Agressive Behavior	0	0	0	0	-	0	0	0	-
Motor Coordination									
↓ Righting Reflex	2	2	4	4	-	5	6	4	-
↓ Hang Response	2	2	5	3	-	6	5	4	-
↓ Posture	0	2	5	4	-	5	5	4	-
C'S									
↓ Startle Response	0	0	0	1	-	0	2	1	-
Tremor, Twitches, Convulsions	0	0	0	0	-	0	0	0	-
Autonomic									
Eyes - ↓ Corneal Reflex	0	0	0	0	-	0	0	0	-
↑ Lachrymation	0	0	5	1	-	0	0	0	-
↓ Clarity	0	1	0	0	-	0	0	1	-
Salivation	0	0	1	1	-	1	1	0	-
Nasal Discharge - abnormal	1	1	3	4	-	4	1	3	-
Visible Respiration	3	0	1	3	-	1	3	4	-
Piloerection	0	0	0	0	-	0	0	0	-

Table 7. Summary of the Observations on the General State of Rats Immediately Following Exposure to the Nonflaming and Flaming Combustion Products of a Bismaleimide Resin.

Number of animals showing abnormal responses.

Observations (group size)	Flaming					Nonflaming				
Concentration (gm/m^3)	13.2	14.4	28.3	33.0	43.1	4.4	6.0	8.8	17.7	26.5
	(8)	(8)	(8)	(7)	(12)	(8)	(8)	(8)	(8)	(8)
# Incapacitated	0	3	7	7	11	0	5	7	8	8
# Deaths During Exposure	-	0	0	2	6	0	0	0	6	8
Behavior										
↓ Activity	2	0	5	4	6	2	3	5	1	-
↑ Sensitivity to Touch	1	1	4	1	1	3	0	1	0	-
↑ Pain (Tail Pinch)	2	3	3	1	4	2	1	0	1	-
↓ Nuzzle Response	1	0	2	0	1	0	1	0	1	-
Agressive Behavior	0	0	0	0	0	0	1	0	0	-
Motor Coordination										
↓ Righting Reflex	3	1	2	1	2	2	2	2	2	-
↓ Hang Response	2	2	6	4	3	0	4	3	1	-
↓ Posture	2	1	5	2	4	0	0	4	1	-
CNS										
↓ Startle Response	0	1	0	1	1	0	0	2	1	-
Tremor, Twitches, Convulsions	0	0	0	0	0	0	0	0	0	-
Autonomic										
Eyes - ↓ Corneal reflex	0	0	0	0	1	0	0	0	0	-
↑ Lachrymation	3	0	0	1	1	2	3	1	0	-
↓ Clarity	0	0	5	0	0	0	0	0	1	-
Salivation	4	1	5	1	5	4	4	5	2	-
Nasal Discharge - Abnormal	5	5	6	5	6	2	4	5	2	-
Visible Respiration	1	0	7	2	5	0	0	0	0	-
Piloerection	0	0	0	0	0	0	0	0	0	-

Those rats that were incapacitated (loss of the leg-flexion avoidance response) on exposure to the nonflaming combustion products of the epoxy resin showed a decrease in activity and a decrease in motor co-ordination (Table 6). An incidence of mild to moderate lachrymation, nasal discharge and respiratory abnormalities was also observed in some rats exposed to various concentrations of this material (nonflaming). Recovery from these abnormal responses occurred within five days for the majority of rats, with the exception of two (exposed to 1.4 and 2.8 gm/m^3) which showed decrements in motor co-ordination throughout the post-exposure period.

The majority of rats exposed to the flaming combustion products of this material showed a decrease in activity and also in motor co-ordination capability. An incidence of moderate nasal discharge and respiratory abnormalities was again observed, but no lachrymation was recorded. Recovery from the abnormal responses was complete within five days at the most, with the exception of the four rats that died during the post-exposure period.

The involvement of rats exposed to both the nonflaming and flaming combustion products of the bismaleimide resin was similar to that described above (Table 7). There was, however, a higher incidence of nasal discharge and respiratory abnormalities, particularly after exposure to the nonflaming combustion products. An incidence of salivation was also recorded in these experiments. Recovery from abnormal responses occurred within 1-6 days for all rats.

Post-exposure Changes in Body Weight. The changes in body weight in exposed rats are shown in Figures 9-12. The rats surviving exposures

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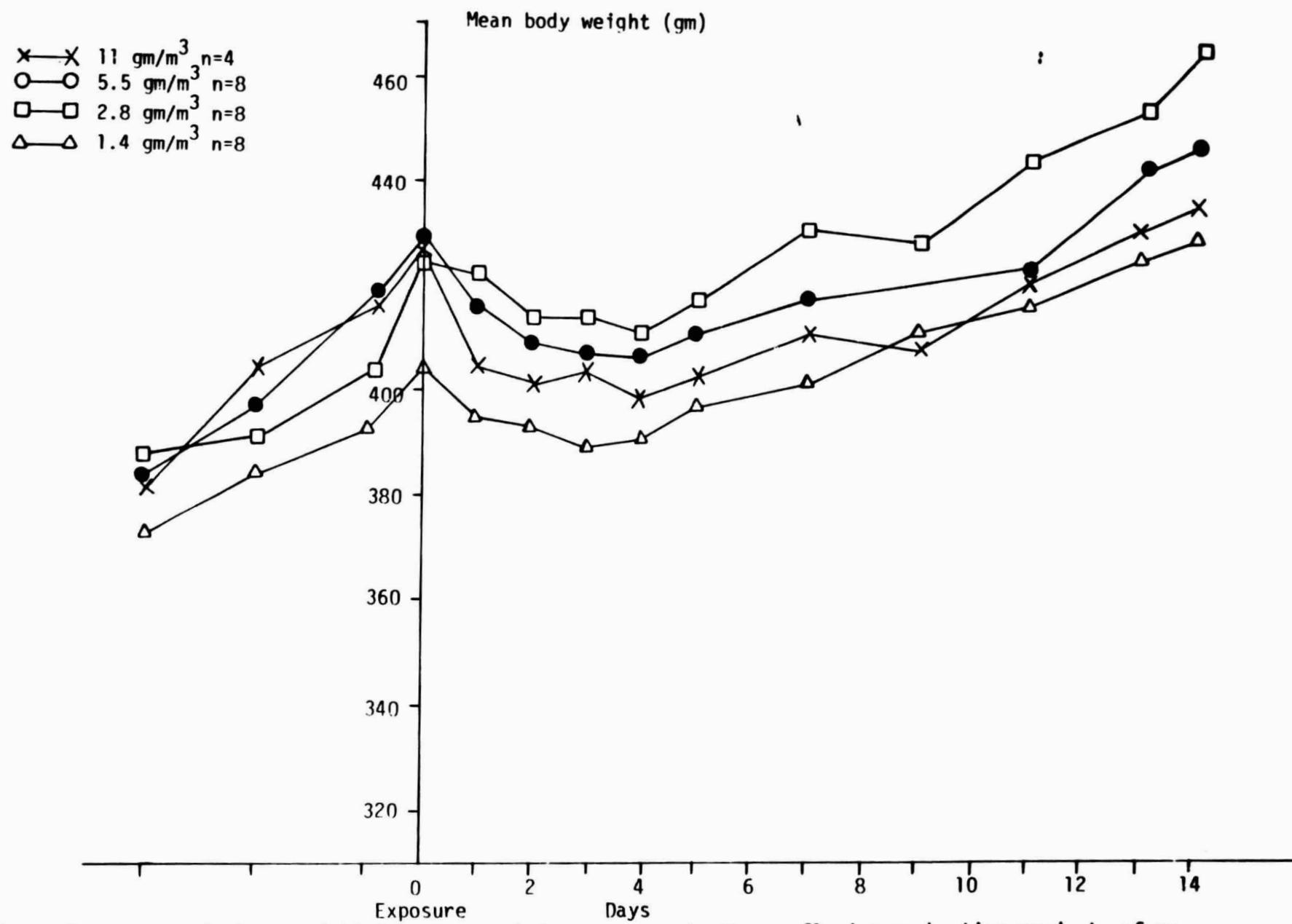
Figure 9. Changes in body weight in rats surviving exposure to the nonflaming combustion products of an epoxy resin.

Figure 10. Changes in body weight in rats surviving exposure to the flaming combustion products of an epoxy resin.

Mean body weight (gm)

3 gm/m³ n=7
5 gm/m³ n=7
11 gm/m³ n=1
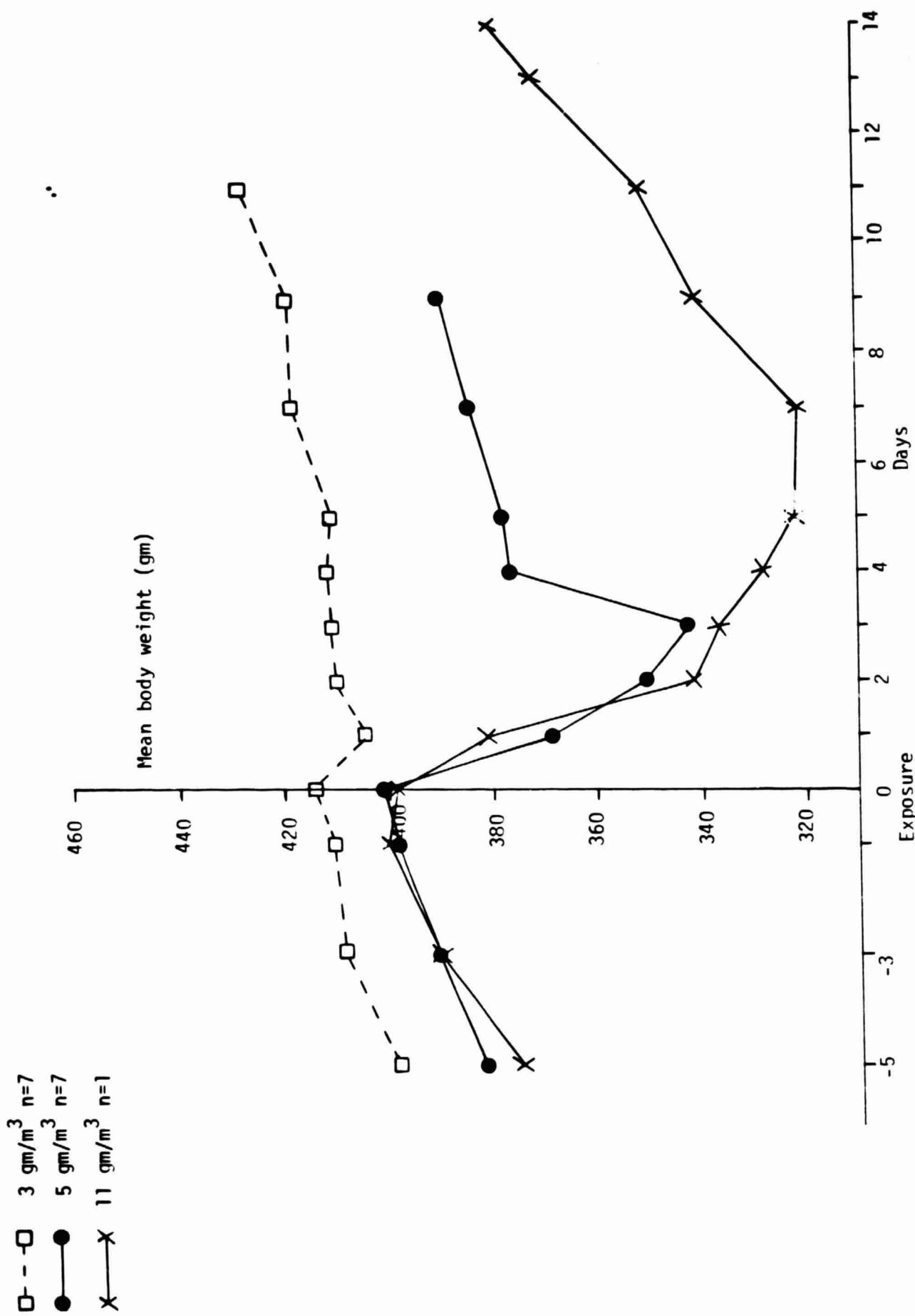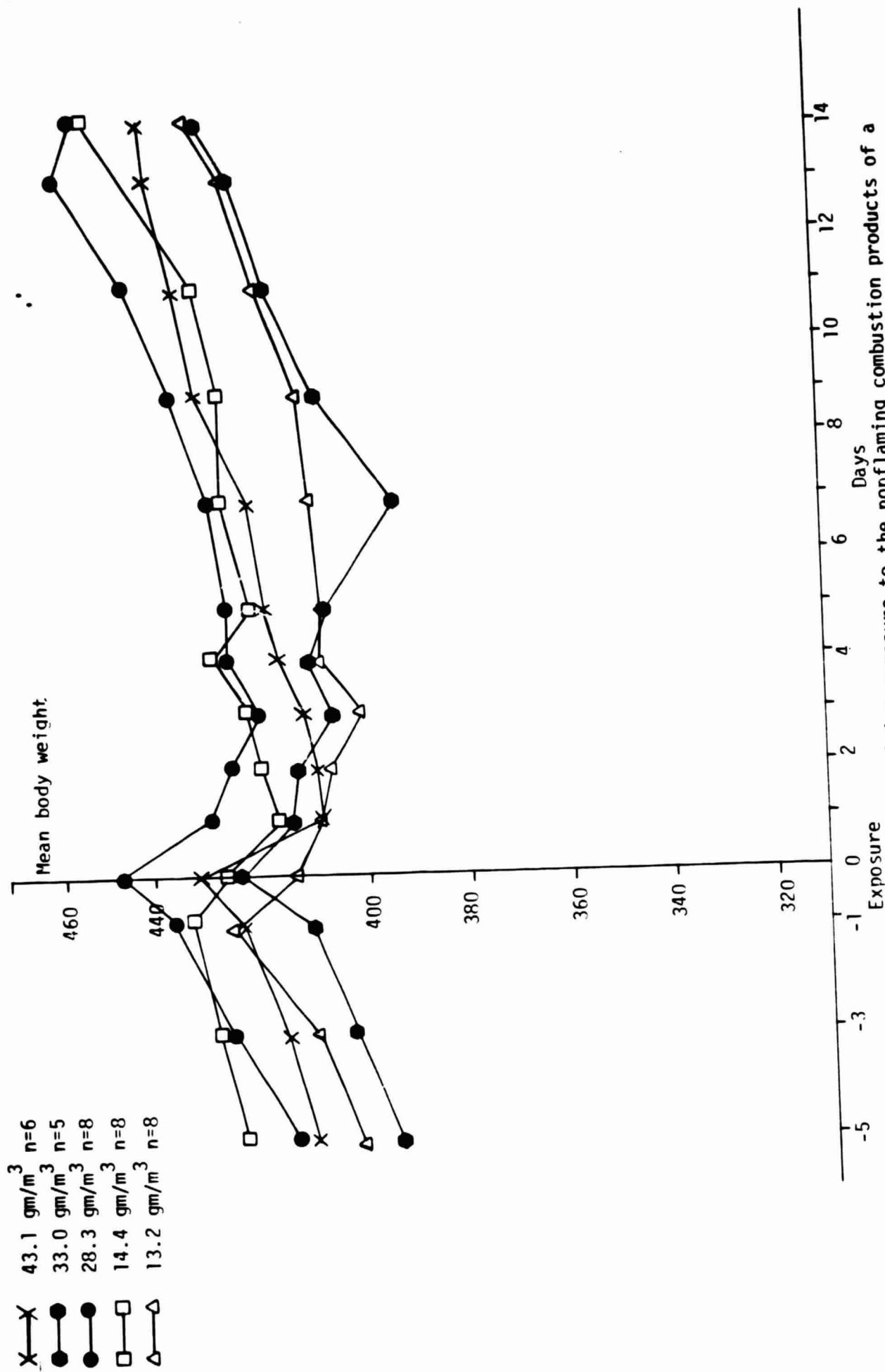
Figure 11. Changes in body weight in rats surviving exposure to the nonflaming combustion products of a bismaleimide resin.
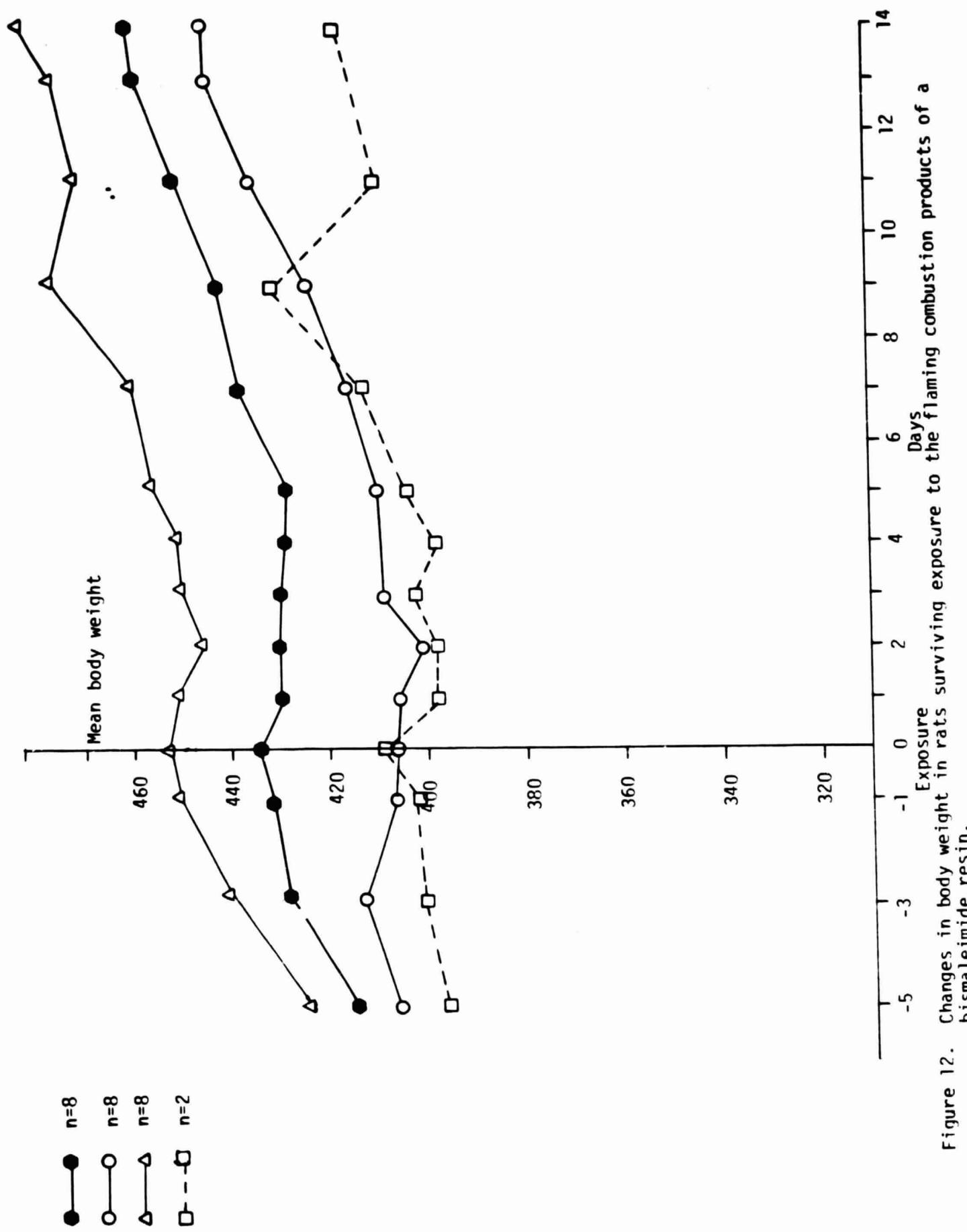
Figure 12.   Changes in body weight in rats surviving exposure to the flaming combustion products of a bismaleimide resin.

to the nonflaming combustion products of the epoxy resin (Figure 9) and also both the nonflaming (Figure 11) and flaming (Figure 12) combustion products of the bismaleimide resin showed minimal changes in body weight during the post-exposure period. These changes were typified by a small fall in weight (less than 5 percent) over the first few days post-exposure, followed by a return to a normal growth pattern.

Rats surviving exposure to higher concentrations of the flaming combustion products of the epoxy resin (Figure 10) showed a more pronounced change in body weight. For example, after exposure to 5.1 gm/m^3 (n=7) the mean body weight in the surviving rats fell approximately 15 percent over the first three days, followed by a return to normal growth.

Gross Pathology. The major observation in those rats that died during the exposure to the nonflaming combustion products of the epoxy resin was the deposition of particles around the nares, in the major airways and the esophagus. Fluid was present in the nares of some of these rats. The lung tissue appeared normal, except for a low incidence of congestion. The only significant observation in rats sacrificed 14 days post-exposure was that of slight congestion.

Those rats that died during the exposure to the flaming combustion products of the epoxy resin showed a greater degree of particulate deposition in the nares, major airways and esophagus. Fluid was also present about the nares and mouth of these rats, and there was slight to moderate congestion of the lung tissue. Four rats died during the post-exposure period. These had severe congestion of the lung tissue. No other significant gross pathological observations were made on these

rats. The only significant observation in rats who survived the 14-day post-exposure period was a low incidence of slight to moderate lung congestion.

Very similar observations were made in rats exposed to the flaming and nonflaming combustion products of the bismaleimide resin. Those rats that died during the exposure had particulate deposition around the nares and slight congestion of the lungs. Those dying on exposure to the nonflaming combustion products also had fluid present about the mouth and nares, and some particulate deposition in the major airways. The only significant observation made in surviving rats was slight congestion of the lung tissue.

Discussion

The relative toxicological potencies of the combustion products of an epoxy resin and a bismaleimide resin have been determined under two ·combustion conditions using an established small-scale experimental combustion/exposure system. By determining both the equi-effective incapacitating (loss of the leg-flexion avoidance response - EC_{50}) and lethal (LC_{50}) concentrations under the two combustion conditions it was found that the EC_{50} and LC_{50} values of the epoxy resin were, for the most part, somewhat lower than the corresponding values for the bis-maleimide resin.

The greatest difference between these values was observed in the nonflaming combustion mode, where the combustion products of the epoxy resin were from four to six times more potent than those of the bis-maleimide resin. The experiment showed, however, that the most toxic environment (lowest EC_{50} and LC_{50} values) for the bismaleimide resin was generated after flaming combustion. In addition, the combustion products of the epoxy resin were somewhat more lethal after flaming combustion. By comparing the worst case toxicity of the two materials, therefore, the potency difference was reduced to a two-fold difference at most. It is normal practice in experiments of this type to consider any difference in EC_{50} or LC_{50} values that is less than a three-fold difference, as insignificant. It is concluded, therefore, that under the conditions of the experiment, and by comparing the worst case toxicity, there was no difference in the potency of the combustion products of the two resins.

Toxicologically significant atmospheric levels of both HCN and CO were generated by both materials under both combustion conditions. Experiments in which rats have been exposed to experimental atmospheres of both of these two toxicants have shown that levels in excess of either 1500 ppm CO [12] or 70 ppm HCN [3] will cause loss of the leg-flexion avoidance response in some of the exposed rats within a 30-minute exposure period. These experiments also showed that rats exposed for 30 minutes to environmental levels in excess of either 3000 ppm CO [12] or 150 ppm HCN [3] are likely to die during the exposure. The effects of the exposure of rats to experimental atmospheres containing various admixtures of these two toxicants in air have not been studied in this laboratory. Other workers have shown, however, that the toxic effects of CO and HCN are at least additive [13]. A review of the atmospheric levels of HCN and CO present in the combustion product atmospheres generated in these experiments shows that the atmospheres resulting from the combustion of 2.8 gm/m^3 epoxy resin (nonflaming), 5.7 gm/m^3 epoxy resin (flaming), 33 gm/m^3 bismaleimide resin (nonflaming) and 6 gm/m^3 bismaleimide resin (flaming) respectively contained at least either 1500 ppm CO or 70 ppm HCN, or both. A role for these two toxicants in the causality of the incapacitation and deaths observed during exposure in these experiments is therefore strongly implicated.

Supportive evidence for the role of CO in these effects can be found in the measured levels of COHb in arterial blood at Ti and at the time of death in individual animals. The exposure of rats to atmospheres of CO in air have shown that both the loss of the leg flexion response and death are associated with discreet levels of COHb in the rat, this being independent of the prevailing environmental CO level. COHb levels

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of approximately 60 percent were found in the arterial blood of in-
capacitated rats at Ti [12], and levels of 80-90 percent were found in
the blood of rats that died on exposure to CO [9]. Combustion product
atmospheres are usually multi-component environments. Because of the
possibility of the slight modification by additional toxicants of the
sensitivity of the rat to CO, particularly in terms of incapacitation,
it has become practice to regard COHb levels in excess of 40 percent to
be of sufficient magnitude to cause loss of the leg-flexion avoidance
response [5]. The majority of rats exposed to the combustion products
of the epoxy resin (both flaming and nonflaming) had COHb levels in
excess of 40 percent at Ti. There were only two exceptions, out of a
total of 18 from which blood data was obtained at Ti. It was concluded
that the levels of inhaled CO were therefore of significant magnitude to
explain the observed incapacitation caused by the combustion products of
this material. The COHb levels at Ti in rats exposed to the combustion
products of the bismaleimide resin, however, were more varied. Although
approximately half of the rats exposed to either the nonflaming or the
flaming combustion products of this resin had COHb levels in excess of
40 percent, the remainder were below this level, and some had very low
COHb levels (<20 percent). The contribution of further toxicants must
also be considered, therefore. With the knowledge that the levels of
HCN in some of these experiments were of sufficient magnitude to cause
incapacitation, it is likely that this toxicant contributed signifi-
cantly to the effect. However, some rats exposed to the nonflaming
combustion products of the bismaleimide resin were incapacitated very
early in the exposure (<15 minutes). Atmospheric analysis showed that
the generation of both CO and HCN in these experiments was delayed. It

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was unlikely that the combined effects of HCN and CO were of sufficient magnitude to cause incapacitation so early in the exposure. Therefore an alternative causative agent must be present in the environment at this time. The chemical nature of this potential incapacitating agent could not be determined from this experiment. However the fact that such a small proportion of the exposed rats were incapacitated early in these exposures, suggested that the presence of this additional agent may not be significant.

The contribution of HCN in the causality of incapacitation in rats exposed to the combustion products of the epoxy resin cannot be totally ruled out. The atmospheric levels of HCN were greater than 70 ppm in most of the combustion product atmospheres generated. It must be re-membered that when CO and HCN co-exist in the atmospheres, both toxicants will be inhaled. Although both HCN and CO cause loss of the leg-flexion response due to hypoxia, the mechanism by which this is achieved differs for each toxicant. CO primarily causes arterial hypoxia by reducing the oxygen-carrying capacity of the hemoglobin through the formation of COHb. HCN, however, causes hypoxia by pre-venting intracellular oxygen metabolism (histotoxic anoxia). Subtle differences in the time-course of these two effects may lead to the masking of the histotoxic effect, by the ongoing loading of CO to the hemoglobin. Similar observations have been made with other materials that generated both CO and HCN as combustion products e.g., isocyanurate foams [1].

The contribution of HCN to the toxicity of the combustion products of both resins was more evident however in rats that died during the exposure. COHb levels measured in these rats were always in excess of

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60 percent, but were not as high as the 80-90 percent measured in rats dying on exposure to CO alone [12]. It was concluded that HCN contributed to the death of these rats, resulting in a lower COHb level than would be anticipated if CO were the only lethal agent present. The presence of CO and HCN did not explain the occurrence of the post-exposure deaths observed in rats exposed to the flaming combustion products of the epoxy resin. The occurrence of these deaths, coupled with the observations of a more pronounced weight loss in surviving rats during the post-exposure period suggested that a further toxicant was present in these atmospheres. The fact that no significant post-exposure effects were observed in rats exposed to the nonflaming combustion products of this resin suggested that either the additional toxicant was not present in these atmospheres or that it was present at toxicologically insignificant levels. Pathological examination of the rats that died during the post-exposure period showed severe lung congestion, suggesting that the lung was the target organ for the additional toxicant. The chemical nature of this toxicant was not determined in this experiment. The fact that the post-exposure deaths occurred at the same combustion product concentrations that were likely to cause deaths during the exposure, suggested that the occurrence of the post-exposure complications did not significantly alter the overall toxicity profile of the flaming combustion products of this resin.

When compared to other materials beyond the scope of this study, the combustion products of both resins were found to be no more toxic than a variety of other materials. For example, the EC_{50} and LC_{50} values for nonflaming Douglas fir combustion products have been determined

to be 4.8 and 14.6 gm/m^3 respectively [1]. In the same study, the flaming combustion products of GM41, an isocyanurate foam, were found to have EC$_{50}$ and LC$_{50}$ values of 4.1 and 11.8 gm/m^3 respectively. The toxicity of the flaming combustion products of the latter material was attributed to the combined effects of HCN and CO. The atmospheric levels of both HCN and CO in the isocyanurate experiments were very similar to those observed with the epoxy resin. However the toxicant generating capacities of the isocyanurate foam after flaming combustion were calculated to be 295 ± 55 mg CO/gm foam and 18 ± 3 mg HCN/gm foam. These values were considerably higher than those calculated for the epoxy resin in the current experiment. This difference is attributed to the high proportion of inert fiberglass present in the laminates of the epoxy resin used in these experiments. An important conclusion that can be drawn from these comparisons is that the two resins did not produce any unusual toxicants, or any highly toxic combustion products other than those normally encountered upon the combustion of materials. Also, there was little evidence for a significant contribution of sensory irritation to the causality of the loss of the leg flexion avoidance response, as has been seen with other materials [1, 3, 5].

The delay in the generation of the combustion products of the bismaleimide resin after nonflaming combustion is an interesting observation. Most materials tested to date in this combustion system behave more like the epoxy resin in terms of the time course of the generation of combustion products. Indeed, this quasi-static exposure system was designed so that the rise time of toxicants from moderate loadings was as rapid as possible (usually within the first five minutes) to allow equilibrium conditions to be achieved quickly within the

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exposure chamber. If the delay in toxicant generation is a property of
the material or the composite, this is an extreme advantage to the
material in terms of its combustion toxicology. When considering the
potential toxicity of the combustion products of the two resins during
the first 15 minutes of exposure, it is likely that there would be a
greater potency difference between the two materials than has been
demonstrated over a 30 minute exposure period. In addition, it is
likely that survival time may be greater upon exposure to the combustion
products of the bismaleimide resin, than with the epoxy resin. This
possibility is supported when comparing the Ti values for individual
animals shown in Figures 7 and 8. The comparison of mean Ti values at
equi-effective concentrations of combustion products did not support
this hypothesis however because of the wide variation in time to re-
sponse in any given group. Time to effect is frequently used for
comparative purposes between materials in similar combustion toxicolog-
ical studies (e.g., 14, 15). However because of the frequent wide
variation in this parameter, it is necessary to interpret this data with
caution.

There are several possible reasons which suggest that the delay in
rise-time of the toxicants generated from the bismaleimide resin might
be artifactual. These are as follows:

1. That it is the result of the use of 490°C as the nonflaming
combustion temperature for the bismaleimide resin. The evidence against
this possibility is that even at 700°C, the flaming combustion temper-
ature, the rise time of CO levels (but not of HCN) was considerably
delayed when compared to the epoxy resin.

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2. That it was the result of the sample configuration. Normally, samples are cut such that the bulk of the sample is distributed equally within the sample beaker, and it is also ensured that samples fall to the bottom of the beaker. This was not possible with either of the materials used in this experiment because of the configuration of the original sample (flat glass laminates) and also the high loadings of material required to generate the combustion products. The fact that the epoxy resin generated its toxicants in the more usual manner, despite the sample configuration used, suggested that this was not the reason for the abnormal behavior of the bismaleimide resin.

3. That it was an artifact resulting from the method of combustion used in these experiments, which relies primarily on conductive heating. It would be of value to study and compare the toxicant generation from the two materials using a different heat source, e.g., radiant heating. It was interesting to note that the time to reach maximal specific optical density in the NBS Smoke Density Chamber, which relies upon radiant heat as the combustion source, was longer for the bismaleimide resin than for the epoxy resin (Section III). This was particularly noticeable at 5 watts/cm^2. This observation may have some relevance to the above reasoning.

Assuming that the observation in the current experiment was not artifactual it still remains a possibility that the effect may be related to the fact that the prepregs tested were constructed using fiber glass. It is proposed to form laminates of graphite fiber with the resin. In the final analysis, the toxicant generation from the material in its final form must be investigated to determine whether the observation is of real value. If toxicant generation were still delayed,

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and was a direct result of the mechanism of thermal decomposition of the resin, the property would remain a distinct advantage of the polymer. The consequences of the property in terms of potentially increased survival time should then be studied in more detail and exploited to its full extent.

In summary, these experiments have shown that there was no significant difference between the toxicological potencies of the combustion products of an epoxy resin and a bismaleimide resin. They also showed that the two materials did not generate any unusually toxic or highly potent combustion product other than those normally encountered. The causality of the observed toxicity of the combustion products of both materials was explained for the most part by the presence of both CO and HCN in the combustion product atmospheres. There was a low incidence of incapacitation in the rat very early in the exposure to the nonflaming combustion products of the bismaleimide resin. There was also a low incidence of post-exposure complications in rats that survived exposures to the flaming combustion products of the epoxy resin. The respective causalities of these effects were not understood, but they were regarded as being of sufficiently low incidence as to not signficantly influence the overall toxicity profile of the combustion products of the two materials. There was no evidence for the presence of toxicologically significant levels of a sensory irritant in the combustion product atmospheres produced from either material. There was, however, some evidence that the survival time on exposure to the nonflaming combustion products of the bismaleimide resin was greater than for the epoxy resin. This was the result of a delay in the generation of the primary toxicants

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(CO and HCN) from this material. This observation may have been an artifact of the experimental conditions. It is of sufficient importance, however, to warrant further investigation to establish the relevance of .the observation to occupant survivability in the post-crash fire scenario in aircraft.

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Acknowledgements

Appendix A

IN-LIFE OBSERVATIONS AND BEHAVIORAL EXAMINATION

APPENDIX A

The following is a description of each part of the daily post-exposure examination given to each animal on a daily basis. Along with the observation description are the grading criteria of the test. The report sheet is shown in Figure 1.

Behavior

-Activity- Subjective opinion derived from experience.

- N - Normal--exploration of and reaction to surroundings.
- ↓ - Decreased--less than normal activity for animal.
- ↑ - Increased--hyperactivity increase in motion and reaction to surroundings.

0 or - - No activity or reaction to surroundings.

-Sensitivity to touch- The animals reaction to being handled.

N or + - Normal.

- ↑ - Increased sensitivity, vocalization, agression.
- ↓ - Decreased sensitivity, inability to respond.
- - - No response.

-Pain--Tail Squeeze- Pinching of the tail ∿ 2" from the end.

N or + - Normal--movement away from stimulus.

- ↓ - Decreased response, acknowledges stimulus but reduced escape response.
- ↑ - Increased response, agression, vocalization.

0 or - - No response.

-Nuzzle-

- + - Animal acknowledges something in front of nose, sniffs about it, explores up and down it.
- ↓ - Decrease--acknowleges presence but no exploratory action about object.
- - - No acknowledgement of anything.

-Agressive Behavior- Subjective as to whether or not the animal exhibits the agressive role in response to being handled.

   + - Exhibits behavior.

   - - Normal or no agressive behavior observed.

-Preening- The animal's normal hygienic, cleaning of the coat.

   + or N - Normal--animal kept.

   ↓ - Some evidence of a reduction in the cleaning by the animal.

   - - Animal unkept, coat chowing accumulation of feces, urine, salivation, nasal discharge, etc.

Motor Coordination

-Righting Reflex- When the animal is held on its back and released approximately 18 inches above the bench top.

   5 - Normal--turns, plants all four feet in time.

   4 - When coming around does not always get all four planted. One may not make it in time or be delayed behind other feet.

   3 - Two or maybe three feet get planted, never four or even close to four.

   2 - Animal might plant one foot, usually lands on side.

   1 - Animal lands on back or maybe slightly on side.

   0 - No response, thud to the table.

-Hang- Balance being held by tail.

   5 - When held by tail animal arches back, extends limbs, makes attempts or does crawl up its tail.

   4 - Arch missing but feet extended. Some movement, climbing up tail, etc.

   3 - Arch missing, feet extended, no motion.

   2 - Arch missing, feet close to body, no motion.

   1 - Everything hangs.

-Posture- Not during motion or movement.

   5 - Normal--back arched up, all feet firmly planted.

   4 - Arch is absent from the back, but feet are planted, body supported by feet.

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3 - Arch absent, feet under animal but supporting no weight, animal lying on stomach.

2 - Animal splaid but making attempts to place feet underneath.

1 - Animal splaid with little or no attempt at support.

0 - Lies in any position placed.

. -Muscle Tone- Subjective.

N - Normal.

↓ - Reduced, strength is reduced, the ability to grasp or exert pressure is reduced.

0 - Animal unable to move.

CNS Involvement

-Startle- Animal's reaction to a hand clap.

+ - Animal starts.

↑ - Animal starts but overreact, jumps in the air, etc.

↓ - Animal reacts but does not startle.

- - No reaction.

-Tremors- Visible tremors.

+ - Present.

- - Not present.

-Twitches- Visible twitching.

+ - Present.

- - Not present.

-Convulsions- Visible convulsing.

+ - Present.

- - Not present.

Autonomic

-Corneal Reflex-

+ - Closes eyelid when cornea touched.

- - No reaction to cornea being touched.

-Salivation- Fluid discharges from the mouth.

> \+ - Present.
>
> \- - Not present.

-Nasal Discharge- Fluid discharges from the nares.

> \+ - Present.
>
> ++ - Slight amount of discharge, but present.
>
> \- - Not present.

-Visible Respiration-

> N - Normal breathing, rate quality.
>
> + - Increased rate.
>
> lb - Decreased rate, harder time breathing, labored breathing.
>
> rb - Respiratory distress.
>
> ab - agonal breathing, severe respiratory distress, gasping, head back, gasping for air.

-Piloerection-

> \+ - Present.
>
> \- - Not present.

Animal Number _____

Ear Tag _____

Exposure Number _____

Date of Exposure _____

Days Post-Exposure	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Behavior Activity														
Sensitivity to Touch														
Pain - Tail Squeeze														
Nuzzle														
Aggressive Behavior														
Preening														
Motor Coordination Righting Reflex 0↔5														
Hang 0↔5														
Posture 0↔5														
Muscle Tone														
CNS Startle														
Tremors														
Twitches														
Convulsions														
Autonomic Corneal Reflex														
Salivation														
Nasal Discharge														
Visible Respiration														
Piloerection														

Notes:

Legend:

N - Normal
↑ - Increased
↓ - Decreased

+ - Present
- - Absent
lb - Labored Breathing

FIGURE. 1